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THE ACTION OF METALS ON NITRIC ACID.

4. THE REDUCTION OF NITRIC ACID BY SILVER.

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In previous articles[1] an attempt has been made to determine the nature of the action between nitric acid and copper, lead, and silver, with the view of throwing light on the so-called theory of reduction by nascent hydrogen. It was shown that silver and copper have substantially the same action, although copper, with dilute acid, produces some nitrous oxide, which is not formed in the case of silver. On the other hand, with lead the volume of the latter gas is much larger, accounting for from 15 to 70 per cent of the metal dissolved, according to the dilution of the acid. Although, in the case of these three metals, we have considerable variety of action, it was thought best to extend the investigation to a metal still more positive than lead, and therefore iron was finally selected. The metal was in the form of piano wire and was practically chemically pure. Of this 0.2 gram was used in each determination and, as in our previous work, with a large excess of acid. The methods followed were those already described. The results obtained are given in Table I and also in the

[1] This JOURNAL, **15**, 71; **17**, 18; **18**, 587.

TABLE I.

Action of Iron on Nitric Acid.

No.	Sp. gr. acid.	Temp.	Ammonia. Mgs.	Equiv. iron.	Nitrogen. cc.	Equiv. iron.	Nitrous oxide. cc.	Equiv. iron.	Nitric oxide. cc.	Equiv. iron.	Nitrogen dioxide. Mgs.	Equiv. iron.	Iron found.	Iron taken.	Per cent found.
1	10.5	18	11.8	103.7	2.84	18.9	1.84	12.24	22.76	58.5	9.25	3.75	197.2	200	98.6
2	1.05	18	11.9	104.8	2.50	16.7	1.95	13.0	22.1	56.7	2.50	1.00	192.1	200	96.07
3	1.10	18	10.1	88.9	3.56	23.76	2.82	18.77	23.45	60.26	4.9	1.98	193.68	200	96.84
4	1.15	18	7.6	66.7	6.68	44.53	2.73	18.2	25.0	64.2	9.35	3.74	197.54	200	98.77
5	1.20	18	5.3	46.6	5.32	35.40	3.8	25.33	28.63	73.24	17.50	7.01	187.44	200	93.72
6	1.25	18	0.8	7.04	2.73	18.28	2.49	16.56	43.32	111.3	89.24	36.23	189.42	200	94.71
7	1.30	18					2.29	15.24	42.5	109.2	186.8	75.84	200.28	200	100.14
8	1.35	18							39.3	101.0	234.8	95.32	196.32	200	98.16
19	1.40	70							30.8	79.15	282.9	114.9	194.4	200	97.2
10	1.40	70							32.8	83.0	265.9	107.9	190.9	200	95.45
11	1.40	70							8.7	16.6	427.8	173.6	190.2	200	95.1

curves in Plates I and II, with specific gravity of acid as abscissae and per cent of metal equivalent as ordinates.

Discussion of Data.

The reduction products are nitrogen dioxide, nitric oxide, nitrous oxide, nitrogen, and ammonia. When iron is dissolved in nitric acid (sp. gr. 1.40) nitrogen dioxide and nitric oxide are obtained in proportions differing considerably with varying amounts of solvent. Thus in Experiments 9 and 10, in which 7 cc. of acid were introduced, there were 40 per cent of nitric oxide to 60 per cent of the dioxide, while in No. 11, with 10 cc. of acid, the ratio was 10 to 90. These differences, due to the change in the mass of acid, confirm our view, which will be developed below, that nitric oxide, in the action of metals on nitric acid, is solely a secondary product of the decomposition of the dioxide.

As the acid diminishes in strength the variation in the relative amounts of these two products is much like that observed with other metals until a specific gravity of 1.30 is reached, when nitrous oxide is formed in amount equivalent to about 8 per cent of metal dissolved; with acid having a sp. gr. of 1.25 the reaction is further complicated by the appearance of nitrogen and ammonia, the former reaching a maximum at 1.15, and then falling, while the latter (the most important product of the reduction of dilute nitric acid by iron) rises to a maximum at 1.05. The amount of ammonia obtained from acid having a specific gravity of 1.25 is 0.0008 gram, equivalent to 7.04 per cent of the metal dissolved; with acid of specific gravity 1.05 the equivalent is 52 per cent.

These results are not in harmony with those obtained by Acworth and Armstrong,[1] who investigated the action of iron on nitric acid of specific gravity 1.20 to 1.03, approximately. These chemists report only three reduction-products, nitric oxide, nitrous oxide, and nitrogen, in proportions not differing very widely from those obtained by us with the same strength of acid, but their percentage of metalac counted for was low, varying from 64.23 per cent with 1.20 to 44.44 per cent with 1.03 acid. This deficiency of metal is accounted for, 1st, by

[1] J. Chem. Soc., **32**, 79.

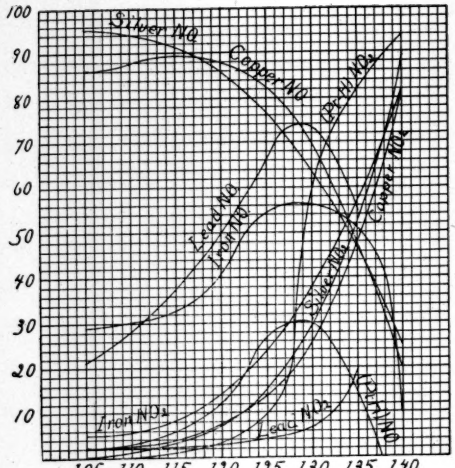


Plate I

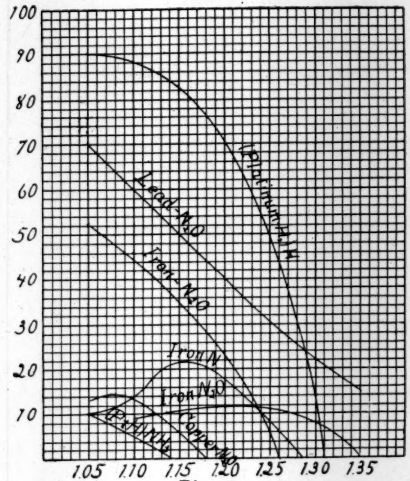


Plate II

NOTE.—In Plate II, in the upper of the two curves marked "Iron—N_2O," for "Iron—N_4O" read "Iron—NH_3."

the fact that nitrogen dioxide was absorbed in the potash bulb which was interposed between the generator and the pump; and 2nd, by the fact that the considerable quantities of ammonia produced from all acid of the above concentrations were overlooked. Take, for example, their result with 1 : 8 acid. If to their per cent of metal (44.44) there be added our metal equivalent of nitrogen dioxide and ammonia (1 plus 52) the sum is 98.4 per cent. A similar, though smaller, correction might be made throughout their whole work with iron.

Silver, copper, and iron have thus a similar action on concentrated nitric acid (1.40 to 1.35), the products being solely nitrogen dioxide and nitric oxide, although in somewhat different proportions; indeed, the curves with silver and copper are throughout nearly identical. The specific action does not become strongly marked until a greater dilution (*i. e.*, greater ionization) is reached. It is evident that the non-ionized acid acts simply as an oxidizer, giving off the least possible quantity of oxygen to form the dioxide, nitric oxide appearing as a secondary product only, in consequence of the action of water on the dioxide. This view is confirmed by the fact cited above, that the relative amounts of these two reduction-products can be varied by changing the mass of the acid. Silver and copper also have substantially the same action on nitric acid of medium strength (1.20) giving 10 per cent nitrogen dioxide and 90 per cent nitric oxide. Lead with the same dilution, however, yields nitrous oxide equivalent to about 40 per cent of metal, nitric oxide equivalent to 50 per cent, and dioxide only in the proportion of about 2.5 per cent. It will be observed that the nitrous oxide curve for lead rapidly rises as that for the dioxide falls, but that its nitric oxide curve, at a dilution of 1.27, is as yet at the same point as this product is with silver and copper. This fact strengthens our view that the oxides below nitric oxide are due to a reduction of nitrogen dioxide and not of nitric acid, but that nitric oxide itself is a result of aqueous decomposition. Iron reduces acid of specific gravity 1.20 more completely, as nitrogen and ammonia, equivalent respectively to 17 and 23 per cent, are given off. Finally, with acid of specific gravity 1.05, the differences in the results obtained with the four metals are very considera-

ble. Nitrous oxide is now found in small quantities among the products obtained with copper, but there is none with silver (see Plate II) ; lead produces nitrous oxide equivalent to about 70 per cent of metal dissolved, and iron yields this substance only in small amount (6 per cent). The latter metal is also quite different from lead as well as from silver in that it yields nitrogen and ammonia equivalent to 8 and 52 per cent of metal. Each metal, therefore, has its own specific action on dilute nitric acid, and, in respect to the degree of reduction, they must be arranged in the following order, beginning with the weakest: silver, copper, lead, and iron. If, however, the concentration of the acid is somewhat greater (1.35), then lead acts more energetically than iron.[1] The metals which produce no oxides below nitric oxide (or at least, as with copper, very little nitrous oxide) have very nearly identical curves for the reduction products which are formed.

The Mode of Action between Metals and Nitric Acid.

It has already been pointed out in discussing the mode of acid between metals and strong nitric acid that the changes are, in all probability, due to direct deoxidation. With more dilute acid, which is ionized to a greater degree, there may be two theories :

1. The metallic atom takes up a positive charge from a hydrogen ion of the metallic salt, while the hydrogen, losing its charge, becomes nascent and effects reduction in different degrees, according to the metal at whose surface it is liberated, and thus becomes capable of either attacking the NO_3 ions of a second molecule or, as seems more probable, of reducing the nitrogen dioxide which has been formed. This may seem but another way of stating the theory of nascent hydrogen in its older form, but that in reality it embodies a notable difference will appear from the work on the electrolysis of nitric acid which follows. The character of the reduction-products and their relative quantities thus depends upon the degree of ioni-

[1] In discussing the action of lead on concentrated nitric acid it must be borne in mind that the metal does not act on acid of a greater concentration than 1.35. Were it to act on the other strengths it is evident from the curve that nearly the same percentage of dioxide would be produced as is obtained with copper and silver.

zation of the acid and also upon the energizing effect of the metal, upon the surface of which the action takes place, the variations being due to the more or less positive nature of the latter.

2. The metallic atoms, acting in conjunction with the hydrogen of a molecule of nitric acid, attack and deoxidize a NO_3 group (or nitrogen dioxide), thus forming water and metallic oxide, the latter neutralizing the acid to produce a nitrate. This second view also contains something of the nascent hydrogen theory. The above considerations made it probable that the effect of electrolytic hydrogen compared with that of copper, silver, lead, and iron acting on the same strength of acid might give results which would go far toward settling the question as to which of these two modes of action is the more probable. If the first is correct, *i. e.*, if hydrogen alone, occluded and energized by the undissolved metal, is the reducing agent with dilute acid, then an electrolysis of the same acid in cells provided with anodes of platinum and with kathodes of silver, copper, and lead, respectively, should at the latter poles yield products differing qualitatively and quantitatively somewhat as do those obtained by the solution of the same metals without the electric current, the acid being of the same specific gravity. For example, lead has been shown to be a much more energetic reducing agent than silver. Suppose two cells, filled with nitric acid of specific gravity 1.05, to be provided with anodes of platinum and kathodes of silver and lead having equal area; if now, on passing a current through these cells in series, the reduction-products are found to be substantially the same, both qualitatively and quantitatively, then, since the action of metal ions is excluded and the reduction is effected by hydrogen ions in contact with the respective metals, the proof would be fairly satisfactory that the wide differences observed in the results of the solution of silver and lead in nitric acid of specific gravity 1.05, are not due to the action of nascent hydrogen. On the other hand, if the products in these two cells should differ widely, those at the lead kathode containing relatively less oxygen than those found at the one formed of silver, this

would indicate the participation of metal atoms in the reduction of nitric acid.

It was therefore decided: 1st, to investigate the action of electrolytic hydrogen upon all the strengths of nitric acid which had been employed in the preceding work, and 2nd, to determine the relative action upon acid of specific gravity 1.05 of electrolytic hydrogen, liberated at kathodes of platinum, silver, copper, and lead.

5. THE ELECTROLYSIS OF NITRIC ACID.

This is not an untrodden field. Faraday[1] has shown that when strong nitric acid is electrolyzed, no hydrogen appears at the kathode, but that, on the other hand, a yellow or reddish color, probably due to nitrous acid, is seen. A different result was, however, obtained on mixing the acid with an equal or greater volume of water, for then hydrogen was produced, the amount of the gas depending both upon the concentration of acid and upon the current employed. To use Faraday's own words, "that acid from which no gas separated at the kathode with a weak voltaic battery, did evolve gas there with a stronger; and that battery which evolved no gas there with a strong acid, did cause its evolution with an acid more dilute."

A little later Schönbein[2] made a series of determinations of the action of electrolytic hydrogen on nitric acid ranging from 1.49 to 1.07 in specific gravity, his object being to determine the conditions under which there is complete oxidation of the hydrogen. Bourgoin[3] subsequently confirmed Faraday's results with concentrated acid, but found that when dilute nitric acid is electrolyzed, some nitrogen and nitric oxide, as well as considerable quantities of ammonia, are produced. Gladstone and Tribe[4] also electrolyzed acid of specific gravities 1.40, 1.20, and 1.13, respectively, employing various current densities. These investigators found that from the first concentration, neither ammonia nor hydrogen was obtained with

[1] Phil. Trans., 1834, 96.
[2] Pogg. Ann., **47**, 563.
[3] Jour. Pharm. (4), **13**, 266.
[4] J. Chem. Soc., **35**, 172.

any current employed; with the second neither of the above compounds was evolved when a current from a single Grove cell was used, but with increased current density hydrogen was obtained. The third gave a reduction of about 50 per cent of the theoretical at the kathode, when two cells were used, but this number fell to less than 1 per cent when eight cells were employed, the hydrogen in this last case being about 98 per cent of that required by theory. No ammonia was detected.

Subsequently Ihle investigated[1] the conditions favorable to the formation of ammonia during the electrolysis of nitric acid. By greatly varying the area of the platinum kathode, he found that an increase in the current density caused an increase in the ammonia formed, but that with given current density the amount of this substance diminished with increasing concentration of acid.

Experimental Part.

The apparatus employed consisted of a large U-tube provided with electrodes of platinum wire ¼ mm. in diameter, fused into the glass and bent into a flat spiral. The kathode was 65 mm. in length, and had therefore an area of about 50 square mm. A few centimeters below the kathode a narrow glass tube was sealed into the U-tube, and through this a current of carbon dioxide was admitted. The reduction-products and the hydrogen were passed through concentrated sulphuric acid, and all gas that remained unabsorbed was collected in a Schiff azotometer over caustic potash (1 : 1). The necessary connections of the apparatus were of ground glass. The gases were analyzed in all respects as described in the previous papers; the relative amounts of nitric oxide and dioxide absorbed by the sulphuric acid being determined by titration with permanganate, and the total nitrogen as nitric oxide by means of the nitrometer. Hydrogen was found by explosion with an excess of oxygen, and ammonia by titration with standard acid. The results of the work are shown on Plates I and II and in Table II.

[1] Ztschr. physik. Chem., **19**, 572.

TABLE II.

No.	Sp. gr. acid.	Current.	Voltammeter. Hydrogen. cc.	Hydrogen.	Per cent.	Ammonia. Mgs.	Per cent.	Nitric oxide. Mgs.	Per cent.	Nitrogen dioxide. Mgs.	Per cent.
1	1.40	0.100	20.8							81.3	93.3
2	1.40	0.100	34.8							82.8[1]	
3	1.35	0.100								109.5[1]	
3[1]	1.35	0.010								26.5[1]	
4	1.35	0.100						4.79	13.8	135.4	86.2
5	1.30	0.100		3.0	9.9			8.6	30.8	75.9	59.3
6	1.25	0.100	34.8	17.9	51.4			8.47	26.7	12.63	8.9
7	1.20	0.100	31.3	24.7	78.9			2.5	8.8	3.81	2.9
8	1.15	0.100	48.7	36.0	73.9			2.9	6.6	3.88	2.2
9	1.10	0.100	25.6	21.46	83.8	0.1	2.03				
10	1.05	0.100	31.32	25.28	80.7	0.6	10.0				
11	1.05	0.100	42.6	35.7	83.8	0.3	5.5				

[1] Cell not heated to expel all products. During the electrolysis the cell was kept at the temperature of the room.

The reduction-product obtained from acid of specific gravity 1.40 was pure nitrogen dioxide.[1] This was the case both when the cell was heated, after the current had been turned off, to expel all the gaseous products (Experiment 1), and also when an analysis was made of those gases only which were swept forward by carbon dioxide at the temperature of the room (Experiments 2, 3, and 3'). With acid of specific gravity 1.35, attempts were made to determine the effects of widely different current densities (Experiments 3 and 3'). The results were the same—nitrogen dioxide was the sole product. In Experiment 4, however, with the same strength of acid, nitric oxide was obtained in quantity equivalent to about 14 per cent of the total product. This was the most dilute acid which yielded no hydrogen, for when that of specific gravity 1.30 was employed, this gas was freely evolved for some minutes, at the kathode, and then suddenly ceased.[2] The remaining products were nitric oxide and dioxide amounting to 30.8 per cent and 59.3 per cent, respectively, of the total. Acid of specific gravity 1.25 yields a much larger percentage of hydrogen (51.4 per cent), nitric oxide being somewhat, and nitrogen dioxide greatly, diminished; with greater dilution, the amount of both of the latter substances is much less, and they practically disappear when the specific gravity is 1.10. Ammonia was obtained in small amounts with acids of the specific gravities 1.05 and 1.10.

Electrolytic hydrogen then, acts upon concentrated nitric acid much the same as do silver, copper and iron, nitrogen dioxide being the principal product in each case, a fact that supports the view expressed above, that the action consists in direct deoxidation; with acid of medium concentration, however, it behaves (at least with the current density employed by us) quite differently from the metals mentioned, since a large percentage (75 per cent) escapes oxidation. Finally, electrolytic hydrogen in its action upon dilute acid, resembles iron more than any of the other metals with which we have

[1] The fact that the dioxide was not decomposed in these cases is undoubtedly due to the very large excess (20 cc.) of nitric acid present. Had an equal amount of this strength of acid been employed in the parallel experiments with the metals, pure dioxide would undoubtedly have been obtained in each case.

[2] This cessation of the evolution of hydrogen is attributed by Gladstone and Tribe to the action of nitrous acid (*loc. cit.*, 174).

experimented, since a considerable amount of ammonia is produced.

6. COMPARISON OF THE ACTION OF ELECTROLYTIC HYDROGEN LIBERATED AT KATHODES OF PLATINUM, SILVER, LEAD, AND COPPER.

Some preliminary experiments were made in which ammonia was the only product determined. The apparatus employed in this part of the work consisted of four cells made of small beakers, each provided with a diaphragm of unglazed porcelain, with anodes of platinum, and kathodes of platinum, silver, lead, and copper foil, respectively; each electrode had an area of 100 square mm. The cells were filled with nitric acid having a specific gravity of 1.05, and were connected in series with a battery, a millammeter, a voltammeter and suitable resistance. The current employed varied from 0.2 to 0.5 amperes. It was found that the evolution of gas at the electrode of copper was but slight, even when a current of 0.5 amperes was employed, but that given off at the kathodes of lead and of silver was considerably greater.

The results are shown in Table III, in which are given

TABLE III.

No.	Current density: amperes per sq. mm.	Ammonia—milligrams. Calculated from voltammeter.	Found at kathode of: Copper.	Per cent.	Lead.	Per cent.	Silver.	Per cent.	Platinum.	Per cent.
1	0.002	9.04	7.9	87.4	2.7	29.8	2.7	29.8	0.2	2.2
2	0.005	20.8	16.8	80.8	8.7	41.3	5.1	25.5	0.66	3.2

current density in amperes per square millimeter, theoretical ammonia as calculated from voltammeter results, and ammonia as produced at the kathodes of copper, lead, silver, and platinum, with the respective percentages. At the close of one experiment it was found that the platinum kathode was nearly covered with a thin coating of copper, from the accidental contamination of the cell contents with a small amount of copper salt. An analysis of the liquid in this cell showed ammonia to the amount of 65.5 per cent of the theoretical.

Having shown that the production of ammonia is an important result of the electrolysis of dilute nitric acid, whether

copper, silver, or lead is employed as kathode, it seemed desirable to determine the other reduction-products. A series of experiments was therefore made in a modified apparatus, similar to that described above, except as noted later. The kathode had an area of 100 square mm. The results are given in Table IV. As will be seen, the sole products obtained from the reduction of nitric acid of specific gravity 1.05, by electrolytic hydrogen at the surface of kathodes of copper, silver, and lead are nitrogen and ammonia.

The effect of high current density is apparent both in the work with copper and silver. Thus in Experiments 1 and 2, in which a current density of 0.001 was employed, the per cent of ammonia varies from 81.1 to 88.6, while in Experiments 3 and 4, in which the kathode was a wire about 20 mm. in length and 0.5 mm. in diameter, placed parallel to the direction of the current, no nitrogen was collected, and ammonia was recovered, equivalent to 96 to 100 per cent of the theoretical. In the work with silver, similar results were obtained. Experiments 7, 8, and 9 demonstrate this fact, the current density in these cases being comparatively low (0.002 to 0.005) and the result a high percentage of nitrogen (63 to 66) and low ammonia (22 to 27.4). In Experiment 10, in which the kathode was a wire about 20 mm. in length and 0.25 mm. in diameter, placed as described above, the percentage of ammonia rose to 54.5, and that of nitrogen fell to 37.6. These results are in harmony with those of Ihle[1] who used kathodes of platinum.

Conclusions.

1. Silver, copper, iron, and electrolytic hydrogen have nearly the same effect on concentrated nitric acid, nearly pure nitrogen dioxide being evolved.

2. In respect to their action on dilute nitric acid, the order of the metals silver, copper, lead, and iron is that of the potential series.

3. The activity of electrolytic hydrogen depends, in a marked degree, upon the character of the electrode upon whose surface it is liberated.[2]

[1] *Loc. cit.*, 574.

[2] Traube has shown that electrolytic hydrogen acts upon oxygen molecules to produce peroxide at the surface of platinum electrodes, but not at electrodes of carbon.

TABLE IV.

No.	Current.	Current density in amperes per sq. mm.	Voltammeter cc. of oxyhydrogen.	Nitrogen. cc.	Per cent.	Ammonia. Mgs.	Per cent.	Total per cent.	Kathode.
1	0.1	0.001	73.42	1.44	18.3	7.6	81.1	99.4	Copper
2	0.1	0.001	80.47	1.11	10.1	9.1	88.6	98.8	"
3	0.1	[1]	millammeter	0	0	15.4	96.4	96.4	"
			Two hours						
4	0.03	[1]	millammeter	0	0	2.6	100.0	100.0	"
			One hour						
5	0.2	0.002	166.9	13.8	61.9	6.1	28.7	90.7	Lead
6	0.2	0.002	162.9	15.9	73.3	5.4	25.9	99.2	"
7	0.5	0.005	150.6	12.6	62.8	4.60	23.9	86.7	Silver
8	0.5	0.005	143.8	13.0	67.4	4.01	22.0	89.4	"
9	0.2	0.002	154.5	13.2	65.0	5.4	27.4	92.4	"
10	0.1	[1]	millameter	10.3	37.6	9.45[2]	54.5	92.1	"
			Two and one-sixth hours						

[1] Wire kathode employed. Current density very high.

[2] Kathode blackened.

4. Electrolytic hydrogen, in contact with kathodes of copper and of silver, effects reduction of nitric acid in proportion to the current density. (Data are wanting in regard to lead.)

5. When nitric acid having a specific gravity of 1.05 is subjected to electrolysis in cells having kathodes of silver and lead, respectively, on the surface of which kathodes there is equal current density, the reduction products are the same; *i. e.*, nitrogen and ammonia, in approximately the same proportions.

6. Silver and lead, when dissolved in acid of specific gravity 1.05, yield reduction products which are widely different, both qualitatively and quantitatively, since from the silver there is obtained only nitric oxide and nitrogen dioxide equivalent respectively to 95 per cent and 5 per cent of metal dissolved, while with lead the products are nitric oxide, nitrogen dioxide, and nitrous oxide, equivalent in the order named, to 2.5, 7.5, and 70 per cent of metal dissolved.

7. Lead reduces nitric acid of specific gravity 1.05 much more completely than copper, yielding about five times more nitrous oxide than the latter. On the other hand, copper, when made the kathode of an electrolytic cell containing the same strength of acid, has a much greater energizing effect upon the hydrogen deposited upon its surface than is shown by lead under the same circumstances, and produces about three times as much ammonia as the latter. This conclusion is even more emphatically impressed on us by comparison of the results with lead and silver.[1]

8. Since, in the electrolysis of nitric acid with a constant current, the action of metallic ions is excluded, and the reduction must be effected by the hydrogen ions in contact with the surface of the different metals, and since, therefore, the hydrogen ion, in contact with the respective metals, is the sole reducing agent, it follows that the widely different products obtained when lead and silver dissolve in nitric acid cannot be attributed to the action of the hydrogen atoms alone, but must also involve the direct deoxidizing effect of the metals themselves. Undoubtedly with the concentrated, and

[1] It must be borne in mind that the kathodes do not change in weight during electrolysis.

hence not ionized, acid, the metals alone cause the change, but with a greater dilution both metals and hydrogen unite in causing reduction. The theory of nascent hydrogen cannot therefore be held in regard to the stronger acids, in which only nitrogen dioxide and nitric oxide are given off, but, subject to the modifications given above, is undoubtedly valid in relation to dilute acid.

We take this opportunity of thanking Dr. Karl E. Guthe, of the physical laboratory, for his helpful suggestions.

ANN ARBOR, January, 1899.

ON THE DISSOCIATION OF PHOSPHORUS PENTABROMIDE IN SOLUTION IN ORGANIC SOLVENTS.

BY J. H. KASTLE AND W. A. BEATTY.

In connection with other investigations which have been conducted in the laboratory of the State College of Kentucky during recent years, we have often observed that many bromine compounds of the most diverse types possess at least one property in common; *viz.*, that they are yellow in the solid state and dissolve in inert organic solvents, such as chloroform, ether, carbon bisulphide, and the like, with the production of a reddish-yellow solution, which in tint closely resembles a solution of bromine itself. The idea, therefore, suggested itself that in such solutions bromine compounds are either wholly or partly dissociated, or perhaps in many instances decomposed in such a way that bromine itself is set free in the solution, thereby imparting the orange-red color which is characteristic of so many bromine compounds. Among the less complicated bromine compounds exhibiting such properties is phosphorus pentabromide. This can be obtained without difficulty in a state of purity, and in the form of beautiful, yellow, rhombic prisms. When heated in a sealed tube it melts to a dark red liquid, which on being further heated is converted into vapor and dissociated, giving dark red vapors of bromine. As the products of the dissociation pass to the colder parts of the tube they recombine and the original substance is deposited in beautiful crystalline

condition. Phosphorus pentabromide is also readily soluble in carbon bisulphide, chloroform, carbon tetrachloride, etc., with the production of red solutions. This compound was, therefore, selected as probably a good substance with which to begin an inquiry into the causes of such phenomena as those under discussion. A quantity of phosphorus pentabromide was prepared by bringing together phosphorus tribromide and bromine in theoretical proportions by weight. The resulting product was found to consist of both the yellow and the red varieties of the compound, the former largely predominating in amount. It was then purified by sublimation in sealed tubes at the temperature of the water-bath, as the result of which it was obtained in the form of large, well-defined, transparent, yellow crystals. Smaller needle-shaped crystals of the red variety were also often obtained by this method of purification, but only in small amounts. The two varieties were, however, usually found to occupy different positions in the tube, and were never so intimately mixed that they could not be readily separated in transferring to the weighing-bottle. At the completion of the sublimation the sealed tubes were opened, and the best crystals of the yellow variety were transferred as rapidly as possible to a weighing-bottle. In consequence of the great affinity of this compound for atmospheric moisture it was not attempted to preserve it for any length of time, but it was used immediately in the preparation of standard solutions in the solvent under investigation. Further, the standard solutions of the phosphorus pentabromide were not kept longer than one day for fear of alteration by the action of the moisture of the air, so that the effect of long standing on the character of such solutions has as yet not been determined.

Carbon bisulphide was the first solvent investigated. In this solvent phosphorus pentabromide dissolves with great ease to form a dark red solution, which on evaporation in the cold deposits both the red and yellow varieties of the pentabromide. This dark-red solution in carbon bisulphide was found to have exactly the same color as solutions of free bromine in the same solvent; and hence the attempt has been made to measure the extent of the dissociation of phosphorus penta-

bromide in carbon bisulphide by comparing such solutions colorimetrically with solutions of bromine in the same solvent —the strength of the latter being determined by means of decinormal solutions of iodine and sodium thiosulphate. The color comparisons were made in flat-bottomed glass cylinders of exactly the same bore, and having very thin walls. The volumes of the solutions of the pentabromide and the standard solutions of bromine with which it was compared were always made the same for each comparison, so that the depth of color was always measured on the same bulk of solution. The colorimetric method as applied here is by no means free from objections, but for certain dilutions, varying from 1/100 to 1/500 N, it leaves little to be desired in point of accuracy. With more concentrated solutions, however, for example 1/10 N, the depth and intensity of the color was found to be such as to prevent exact comparison with the standard solutions of bromine, by means of the appliances now at our disposal, and hence no measurements at a concentration greater than 1/100 N have as yet been made, and at dilutions greater than 1/1000 N no very exact measurements could be made on 10 cc. portions, on account of the extreme lightness of the tints; and hence no comparisons have been attempted at dilutions greater than 1/1000 N. In fact, as will be seen, from the results obtained at greater concentrations, there does not seem to be any necessity for making these measurements on extremely dilute solutions, inasmuch as the pentabromide seems to be completely dissociated even at much greater concentrations. It is highly important, however, to make these color comparisons at dilutions greater than 1/1000 N, and for this purpose we hope shortly to devise a satisfactory method. The following results have been obtained for the dilutions indicated.

Table I.

Dilution of PBr_5 in carbon bisulphide.	Cc. PBr_5 solution used in each experiment.	Cc. bromine solution required to give the same color as PBr_5.
1/100 N	10	0.5 Sol. I
1/100 N	10	0.9 Sol. II
1/100 N	10	0.9 Sol. II
1/200 N	10	0.85 Sol. III
1/200 N	10	0.9 Sol. III
1/500 N	10	1.7 Sol. IV
1/1000 N	10	0.9 Sol. IV

Quantity of bromine required to give the color of the PBr_5 solution. Gram.	Theoretical quantities of bromine set free in dissociation of PBr_5.	Percentage dissociation.
0.0177	0.0160	110.6
0.0161	0.160	100.6
0.0161	0.160	100.6
0.0075	0.080	93.8
0.0079	0.080	98.8
0.0031	0.0032	96.9
0.0016	0.0016	100.0

Strength Br Solutions Used in Above Table.

Bromine, Solution I contained 0.0354882 gram Br per cc.
" " II " 0.0178915 " " " "
" " III " 0.0087696 " " " "
" " IV " 0.0018009 " " " "

These results certainly seem to indicate that phosphorus pentabromide is completely dissociated in carbon bisulphide solution, according to the equation:

$$PBr_5 = PBr_3 + 2Br,$$

at all dilutions ranging from 1/100 to 1/1000 N, and the view that the change in question is really one of dissociation, and not a non-reversible decomposition, into phosphorus tribromide and bromine finds support in the facts that both the red and yellow crystalline modifications of the pentabromide can be obtained from its solutions in carbon bisulphide. The conduct of pentabromide towards heat in a closed tube, and also the conduct of phosphorus pentachloride in the gaseous state might also be cited in support of this conclusion. And in this connection it should be observed that the formation of such red solutions by phosphorus pentabromide, which itself is yellow, would be extremely difficult of explanation upon any other grounds than those involving the dissociation of the compound into the tribromide and bromine, this latter imparting the characteristic red color to such solutions. The color of phosphorus pentabromide in the solid state at ordinary temperatures is not very different from that of octahedral sulphur. Solutions of sulphur in such solvents as carbon bisulphide, naphthalene, etc., have a yellow color, whereas, as

has been repeatedly stated, similar solutions of phosphorus pentabromide have the red color of bromine. In solutions of sulphur the characteristic yellow color is imparted by molecules of sulphur, whereas the supposition seems justified that in solutions of phosphorus pentabromide the characteristic red color is imparted by molecules of bromine—this latter substance having resulted from the dissociation of molecules of the pentabromide.

It has also been observed in this connection that the addition of phosphorus tribromide to the solutions of the pentabromide in carbon bisulphide causes them to become lighter in color, and conversely solutions of phosphorus pentabromide in the tribromide become darker in color on the addition of carbon bisulphide. This, of course, signifies that the phosphorus tribromide as one of the products of the dissociation exerts a repressive effect on the change in question, and by its presence drives a certain amount of the product of the dissociation into combination, and, as is well known, such phenomena are characteristic of the dissociation process.

Similar experiments have been tried using carbon tetrachloride as the solvent. In this solvent phosphorus pentabromide dissolves to form a red solution, which in tint is exactly comparable with a solution of bromine in this solvent. The results obtained with carbon tetrachloride are given in full in Table II.

Table II.

Dilution of PBr_5 in carbon tetrachloride.	Cc. PBr_5 solution used in each experiment.	Cc. bromine solution required to give the color of the PBr_5 solution.
0.5157 gram PBr_5 in 50 cc. CCl_4.	5	2.8
0.5157 gram PBr_5 in 100 cc. CCl_4	10	2.8
0.3093 gram PBr_5 in 100 cc. CCl_4	10	1.6
0.2062 gram PBr_5 in 100 cc. CCl_4	10	1.1
0.1031 gram PBr_5 in 100 cc. CCl_4	10	0.5

Quantity of bromine required to give the color of the PBr_5 solution. Gram.	Theoretical quantities of bromine set free in complete dissociation of PBr_5.	Percentage dissociation.
0.0175	0.01914	91.4
0.0175	0.01914	91.4
0.0100	0.0115	87.0
0.0069	0.0077	89.6
0.0031	0.0038	81.6

The solution of bromine in carbon tetrachloride used in these measurements contained 0.006264 Br per cc.

It will be seen from these results that in solutions of carbon tetrachloride, as dilutions varying from about 1/40 to about 1/400 N, phosphorus pentabromide is dissociated to the extent of 90 per cent. This would seem further to represent the maximum dissociation of this compound in this solvent inasmuch as no increase in the dissociation was observable in passing from the lowest to the greatest of these dilutions. In fact, as will be seen in the above table, there seems to be a falling off in the dissociation from 91.4 to 81.6 per cent in passing from 1/40 to 1/400 N dilution. This is believed, however, to be due to an error in the colorimetric determination at the greater dilution—the very light tint obtained at this great dilution with this solvent rendering exact comparisons with the standard bromine solution difficult and uncertain. Further, any slight error with such small amounts as are present at this dilution would be considerably magnified in the calculation of results. The fact that the dissociation of phosphorus pentabromide in carbon tetrachloride is less by 10 per cent than in carbon bisulphide, in which latter solvent it was found to be complete, is rather remarkable, and at present no sufficient reason for this has been found. It should be noted in this connection, however, that the solubility of phosphorus pentabromide is considerably less in carbon tetrachloride than in carbon bisulphide. In the former solvent it was found to dissolve only sparingly, whereas in the latter it was very freely soluble. It may be that this difference in solubility will account for the difference in the degree of the dissociation in these two solutions.

As stated above, all of these measurements both on carbon tetrachloride and carbon bisulphide solutions of the pentabro-

mide were made with the freshly prepared solutions, and no differences in color intensity were observable between the freshly prepared solutions and those that had stood for several hours; so that the dissociation equilibrium seems to be reached almost instantaneously, at least, at the dilutions investigated. We hope, however, to make further studies bearing upon this point. The effect of temperature and concentration on the progress of the change will also be studied in the case of solutions of phosphorus pentabromide, of phosphorus trichlordibromide, PCl_3Br_2, and of phosphorus trichlordiiodide, PCl_3I_2. The conduct of these last-named substances should prove especially interesting in this connection.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, Feb., 1899.

ON THE COLOR OF COMPOUNDS OF BROMINE AND OF IODINE.

BY J. H. KASTLE.

It is believed that the results already discussed in the preceding paper on the dissociation of phosphorus pentabromide will, if correctly interpreted, throw some light on the color of halogen compounds. So far as is known to the writer, no one has ever attempted an explanation of the remarkable relations as to color existing among the halogen derivatives. Ostwald[1] has attempted to account for the characteristic color of certain classes of salts in solution by the theory of electrolytic dissociation.

The present writer in 1894[2] called attention to certain difficulties encountered in endeavoring to apply the theory of electrolytic dissociation to the color of salts in solution, and advanced the view that such color could be better explained by supposing such substances to be hydrolyzed in solution whereby greater or less amounts of the colloidal modification of the base would be produced, and this being of itself colored would serve to impart the characteristic color of a given class of salts to the solution itself.

Carey Lea[3] has made the color of the ions of elements the

[1] Theory of Solutions, Eng. Ed., 268. [2] This JOURNAL, **16**, 326.
[3] Chem. News, **48**, 203, 260, 271 (1896).

basis of a system of classification ; and from his study of the color relations of atoms, ions, and molecules he draws several conclusions, the most important of which for the discussion in hand is as follows :

" When highly colored inorganic substances are composed of colorless ions, then if these substances can be brought into solution, the color wholly disappears. A number of instances are given above, and no exceptions were met with. Much that is important follows from this. It is proved that the ions have become so far separated that they no longer influence each others' vibration periods. For example, antimony pentasulphide is an intensely colored substance. It dissolves easily in solutions of alkaline sulphides, forming absolutely colorless solutions, because the ions of antimony and sulphur are colorless, and in the act of solution they separate sufficiently to no longer influence each others' vibration periods, without, however, passing out of each others' spheres of influence. The ion theory is the only one capable of explaining this loss of color ; and, on the other hand, the reactions are so exactly conformable to that theory that they constitute a new proof of its correctness."

In another part of this paper Carey Lea cites mercuric iodide as an excellent illustration of the principle just stated, for the reason that while it is strongly colored in the solid state its solutions are colorless.

Quite recently Venable and Miller[1] have investigated the change in color of solutions of chromic salts from violet to green, and have adopted the explanation originally offered by Berzelius ; *viz.*, that the change in question is brought about by the formation of a soluble basic salt which itself is green in color. A number of explanations have been advanced also from time to time for the characteristic color of certain groups of organic dye-stuffs, but so far as the writer is aware no one has ever attempted to account for the color relations among halogen compounds, generally, or, to take a special case no one has ever made an attempt to account for the fact that lead bromide is white, while the iodide is yellow. The color relations existing among the halogen compounds are so well

[1] J. Am. Chem. Soc., **20**, 484.

known as scarcely to require mention. In order that the subject may be clearly presented and for the purposes of argument, it will be well to enumerate them in this connection. In the first place, it should be clearly borne in mind that the halogen compounds of such elements and radicals as furnish colored compounds generally are beyond the scope of the present discussion; and that the same applies only to those colored compounds, the color of which seems certainly to be due to the presence of the halogen.

Omitting such compounds as those of the elements chromium, nickel, copper, cobalt, etc., and the halogen derivatives of such organic compounds as are in themselves dye-stuffs, or contain a chromogenic group, it would seem that the following general propositions could be laid down concerning the color of halogen compounds:

1st. Nearly, if not all, fluorine compounds are white; a few are colored. For example, bismuth fluoride is described as gray, and one modification of silver fluoride as yellow.

2nd. By far the greater number of chlorine compounds are white; a few, however, are yellow, for example PCl_5, and pentachlorphenolchloride, C_6Cl_5OCl.

3rd. By far the greater number of bromine compounds are white; a considerable number of them are yellow in color; some are red, and quite a number of perbromides are known having a red color.

4th. The greater number of iodine compounds also are white; a considerable number are yellow; and such as are darker in tint than the corresponding yellow bromine compounds, also a few iodides, are red, and a great many periodides are known which show a general resemblance in appearance to iodine in the solid state, and which by transmitted light exhibit the dark wine-red tints, characteristic of iodine in the liquid state and of solutions of this element.

5th. The color intensity of the halogens may be represented roughly at least, by the sign of greater or less, $F<I$, and the color intensity of their corresponding compounds, in some instances at least, may be similarly indicated, $MF<MI$.

The examples given in the following table will serve to illustrate the truth of these general propositions:

Fluorine.

White compounds.	Yellow compounds.	Red compounds.
CaF_2, PF_5		

Chlorine.

Tetrachlorquinone	PCl_3, $C_6Cl_5.OCl$	
$HgCl_2$, NaCl		
NaCl, KCl, $BaCl_2$		
$CaCl_2$, $AlCl_3$,		
$CHCl_3$, AgCl		
$PbCl_2$, HgCl		
$AsCl_3$, $SbCl_3$, PCl_5		
$C_6H_6SO_2NCl_2$, $C_4H_8.OCl$		
CCl_4, $Cl.5H_2O$, etc., etc.		

Bromine.

KBr, NaBr, $CaBr_2$	AgBr, $C_6H_5.SO_2NBr_2$	$Br.5H_2O$
$BaBr_2$, $HgBr_2$, $PbBr_2$,	$C_4H_3B_3OBr$	KBr_3
$CHBr_3$, CBr_4, PBr_5	HgBrI, PBr_5	
	CBrO	

Iodine.

KI, NaI, CaI_2	AgI, HgI_2	CI_4, PI_3
BaI_2, etc.	HgBrI, PbI_2,	KI_3, HgI_2
	CHI_3, HgI	AsI

The gradation in color which is often observed among halogen compounds is well illustrated by the following series of compounds :

AgCl—white	$CHCl_3$—colorless
AgBr—light yellow	$CHBr_3$—colorless
AgI—yellow	CHI_3—very light yellow
CCl_4—colorless	$HgCl_2$—white
CBr_4—colorless	$HgBr_2$—white
CI_4—dark red	HgBrI—very light yellow
	HgI_2—yellow or red
$PbCl_2$—white	PF_5—colorless
$PbBr_2$—white	PCl_5—light yellow
	PBr_5—yellow or red
PbI_2—yellow	PI_5—not known with certainty

From even these few examples one thing seems reasonably certain, and that is that the color relationships displayed among halogen compounds are not haphazard, nor mere coincidences, but are as much the subject of law and order as any other properties of compound substances. Whether any sat-

isfactory explanation can be offered for these relationships as to color remains yet to be seen. It is believed, however, that the color and general conduct of phosphorus pentabromide and similar compounds is such as to throw considerable light on this subject. Phosphorus pentabromide is a yellow crystalline compound slightly darker in tint than octahedral sulphur. It has been described as having a citron-yellow color. When this compound is heated in a sealed tube it becomes darker and more red in color and then melts to a red liquid, which at once dissociates, filling the tube with deep-red vapors, exactly the color of free bromine, and from these vapors the compound is deposited in beautiful crystalline condition on the colder parts of the tube. Now let us reverse this process, and start with a hot tube filled with the dissociated vapors of this compound, and so cool that the compound will first condense to a liquid, which will then solidify, giving us the yellow crystalline variety of the compound. The color is certainly such that on looking at a heated tube containing this substance in which the contents are gaseous no one could doubt for a moment that bromine as such is present in gaseous form, and that the red color of the gases is in reality due to this constituent. But this compound is also red in the liquid state. Hence, if we believe that the red color of this substance in the gaseous state is due to the presence of free bromine, it seems probable that free bromine is present in the substance in its liquid condition, or that it is dissociated in the liquid as well as in the gaseous condition, only not to as great an extent. Finally the red liquid solidifies and a yellow crystalline substance results. To what is the yellow color due? To free bromine or to the compound itself? If there is anything in common between the solid, liquid, and gaseous states, and the kinetic theory certainly indicates that there is a great deal in common between them, it again seems not improbable that this yellow color is due to bromine. It would certainly seem to be in keeping with our knowledge of the continuity of the gaseous liquid and solid states to suppose, if the dissociation of any substance takes place to a very large extent in the gaseous condition and also to a notable degree in its liquid state, that it will also occur in

smaller amount, at least, even in the solid state; and, hence, if it can be shown that the color of the substance in the gaseous state is due to one of the products of its dissociation, and the same for its color in the liquid condition, it would seem to follow logically that any similar color it might possess in the solid state is due also to the presence of one of the products of dissociation in smaller amount than in the liquid or gaseous condition of the substance. All this, of course, implies that the color of the substance is essentially the same in tint in the solid, liquid, and gaseous states, or that the product of the dissociation producing the color is capable of exhibiting two distinct color tints. In the solid state the yellow variety of phosphorus pentabromide has but little, if anything, of the reddish tint of bromine. The question then is, is there anything in common between the yellow color of this compound and the color of free bromine, or, stated in still another way, does free bromine ever impart a yellow color? In the first place, bromine vapor has been described as yellowish-red, and it gets more highly colored on heating; and then it is believed that the answer to this question is also to be found in the color of aqueous solutions of this element. It can scarcely be called in question that the bromine in aqueous solutions at ordinary temperatures is chemically in the free condition, for according to investigations of Löwig[1] even the orange-colored hydrate of this element is dissociated at all temperatures above 15° C.; and yet it is a fact that an aqueous solution of bromine is altogether different in color from a solution of this element in such solutions as carbon bisulphide, chloroform, etc.

An aqueous solution of bromine has a pronounced yellow tint which is not observed in solutions of this element in organic solvents; in fact, as was observed in this laboratory several years ago, very dilute aqueous solutions of bromine show the most striking resemblance to strong chlorine water when the two are compared in long porcelain tubes, so that bromine, which is free in a chemical sense, may exhibit a yellow color, which is very much the same in tint as the yellow color shown by such substances as phosphorus pentabro-

[1] Pogg. Ann., **14**, 114; and **16**, 375.

mide and other yellow compounds of bromine and iodine. This change in the color of aqueous solutions of bromine from red to yellow is also observed by adding potassium bromide to the solution. This of course might be interpreted to mean that potassium perbromide is produced which in solution has a lighter and more yellow color than bromine itself. This is doubtless true, but the question suggests itself at once what constitutes the difference in color between potassium bromide, which is white, and this compound, which has been described by Berthelot as being orange-colored? There can be but one answer to this question, and that is that the difference in color is due to the molecule of bromine which differs from the other atom of this element in the compound, in that it conducts itself like free bromine; and then again from what has been shown by Jakowkin[1] regarding the conduct of potassium periodide it is certainly probable that this compound KBr_3 is largely, if not entirely, dissociated in its aqueous solution; so that in this case as with the bromine hydrate and aqueous solutions of bromine there is a characteristic chemical instability, and a yellow color, both of which are traceable to what we ordinarily call free bromine.

In this connection it should be borne in mind also that all that has been said regarding the yellow tint observable in free bromine applies with equal force to the element iodine. Very dilute aqueous solutions of iodine also exhibit a yellow tint in every way analogous to that observed in solutions of bromine; and the effect of adding potassium iodide to dilute aqueous solutions of iodide is to bring out this yellow color strongly.[2]

[1] Ztschr. physik. Chem., **13**, 539, and **20**, 19.

[2] The influence of potassium iodide on the color of an aqueous solution of iodine is very remarkable, as is also the influence of potassium bromide on the color of an aqueous solution of bromine. These two salts in concentrated solutions have the effect of doing away, to a large extent, with the reddish tints of iodine and bromine, and making solutions of these elements decidedly more comparable with a solution of chlorine in color. The attempt has been made to determine roughly the color intensity of chlorine, bromine, and iodine by comparing strong chlorine water with very dilute solutions of bromine and iodine in concentrated solutions of potassium bromide and iodide respectively. The following are the results of some preliminary work in this direction:

The chlorine water used contained 0.00594204 gram per cc.

The bromine water used contained 0.000499527 gram per cc.

The iodine water used contained 0.00022015 gram per cc.

The solution of potassium iodide contained 150 grams KI in 250 cc. aqueous solution.

It has also been observed in this connection that, if solid iodine is reduced to a fine powder and mixed with an inert substance, such as dry finely-divided silica, a mixture is obtained which exhibits a decidedly yellow color, although the reddish tint of the iodine is also observable. If now it can be assumed that a somewhat similar condition of things exists, within solid crystalline bromides and iodides, we have a satis-

The solution of potassium bromide contained 80 grams in 250 cc. solution.

The following are the results of experiments made on the color of the iodine solution :

0.05 cc. iodine solution, imperceptible in 20 cc. of water, gives a distinct yellowish coloration with 20 cc. KI solution.

0.1 cc. iodine solution, equivalent to 0.000022015 gram iodine, is scarcely perceptible in 20 cc. of water.

0.1 cc. iodine, equivalent to 0.000022015 gram iodine, is distinctly yellowish in 20 cc. concentrated solution of KI.

0.2 cc. iodine solution, easily perceptible in 20 cc. of water ; giving a sort of reddish-violet tint to the solution.

0.2 cc. iodine solution, darker yellow than that produced with 0.1 cc. iodine solution in 20 cc. solution of KI.

0.3 cc. iodine solution, equivalent to 0.000066045 gram iodine, had fully as much color in 20 cc. of KI solution as 20 cc. of the chlorine water, the latter containing 0.1188408 gram of chlorine. The general resemblance to chlorine water of such a solution of iodine in potassium iodide as this is quite striking, but, in addition to its distinct greenish-yellow tint, it also shows a reddish-brown tint, which makes it impossible to produce exactly the same shade in the two. According to this experiment, the color intensity of chlorine and iodine would be as 1 to 1799.

Similar experiments made with bromine gave the following results :

0.3 cc. bromine solution, equivalent to 0.000149858 gram bromine, imperceptible as compared with 20 cc. of water.

0.5 cc. bromine solution, perceptible in 20 cc. of water.

1 cc. bromine solution, easily perceptible in 20 cc. of water ; slight brownish color.

2 cc. bromine solution, equivalent to 0.000999 gram bromine in 18 cc. KBr solution had almost the same tint as 20 cc. of the chlorine water—this latter containing 0.1188408 gram of chlorine, the only difference observable in these two being a slight reddish tint in the bromine solution which was not observed in the chlorine water. According to this experiment the relative color intensity of chlorine and bromine would be as 1 to 118.

Hence we have for the relative coloring power of these three elements the following : Cl, 1 ; Br, 118 ; I, 1799.

From these numbers it will be seen that there is a much greater difference in coloring power between chlorine and bromine than between bromine and iodine, and that such indeed is the case, seems to be indicated by many facts pertaining to the color of these three elements. From the numbers above given it will be observed that the color intensity of bromine as compared with iodine is about in the ratio of 1 to 15. By comparing the amounts of bromine and iodine, which are the smallest quantities perceptible in 20 cc. of water, the ratio of the color intensity of these two elements was found to be as 1 to 13.6. So that it would seem to be not far from the truth to say that in coloring power iodine is fifteen times as great as bromine. In this connection it should be stated that Schütze has already called attention to the fact that in the case of analogous elements an increase in atomic weight is attended by a deepening of color. It will be seen from the above, however, that the increase in color intensity is greatly in excess of the corresponding increase in atomic weights.

factory explanation of a large number of facts pertaining to the color of these compounds. It has been demonstrated beyond question that there is a causal connection between the dissociation phenomena of compound substances and the affinity of the elements composing them. The affinities of elementary substances are inversely proportional to the ease with which their compounds undergo dissociation. We are in the habit of attributing the difference in the conduct of hydrochloric and hydriodic acids towards heat to the different affinities of chlorine and iodine for hydrogen. So in the same manner it has been observed that these halogen compounds are the more highly colored which are the least stable and whose elements are held in combination by weaker affinities.

A great number of samples could be furnished illustrating the truth of this statement. A few of the more striking instances are given in this connection :

PF_3—colorless, compound stable.
PCl_3—colorless, compound stable.
PBr_3—colorless, compound stable.
PI_3—red prisms ; melts at 55° C. and boils at higher temperatures with evolution of iodine.

$TeCl_4$—colorless.
$TeBr_4$—orange when cold, bright red while hot.
TeI_4—black, gives off iodine when heated.

CdF_2—white, stable.
$CdCl_2$—white, stable.
$CdBr_2$—white, stable.
CdI_2—white and also brownish, brownish variety unstable.

PF_5—colorless, stable.
PCl_5—very light yellow, somewhat unstable.
PBr_5—Light orange yellow, also red ; more unstable than chloride.
PI_5—So unstable that existence is doubtful.

CCl_4—colorless liquid, stable.
CBr_4—white solid, partly decomposed at 200° C. with evolution of bromine.
CI_4—red, must be kept out of air. Decomposed by heat into carbon and iodine, and by water to iodoform.

$CHCl_3$—colorless, stable.
$CHBr_3$—colorless, stable.
CHI_3—greenish-yellow, unstable both toward light and heat.

The same relation between color and instability and the converse, is found to hold also among aromatic compounds. As is well known, substitution of halogens for hydrogen in the ring has been found to produce compounds of remarkable stability. They have also been found to be colorless in nearly all instances. On the other hand, when the halogen enters in a side-chain the compounds produced are frequently unstable and are also nearly always colored either yellow, orange, or red. The following are some of the examples of these two classes of compounds :

Compounds Containing the Halogen in the Ring and Showing great Stability.

Iodobenzene—colorless oil.
Hexachlorbenzene—white.
Hexabrombenzene—white needles.
Pentabrombenzenesulphonic acid—white plates.
Pentabrombenzenesulphonamide—white needles.
p-Chlorbenzenesulphonamide—white needles.
Tribromphenol—white needles.
Tetrabromphenol—white needles.
Pentabromphenol—adamantine crystals.
Triiodoaniline—white needles.
p-Diiodobenzene—nacreous scales.
Triiodophenol—white needles.
Diiodophenol—white glistening plates.
Diiodosalicylic acid—white.
Pentachlorphenol—white needles.
Diazobenzene bromide—white.
Diazotribrombenzene sulphate—colorless.

Aromatic Compounds Containing the Halogen in the Side-chain and Exhibiting Greater or Less Instability.

Tribromphenol bromide—light yellow.
Pentachlorphenol chloride—golden yellow.
Diazobenzene perbromide—yellow.
Diazotribrombenzene bromide—golden tablets.
Diazotribrombenzene perbromide—orange prisms.
Iodobenzene chloride, $C_6H_5ICl_2$—yellow needles. Begins to decompose at 80° C., and decomposes completely at 120° C. into iodobenzene and chlorine.
p-Bromiodobenzene dichloride—yellow needles, unstable.
Benzenedibromsulphonamide, $C_6H_5SO_2NBr_2$—orange yellow, melts with decomposition at 110° C.
p-Chlorbenzenedibromsulphonamide—yellow, unstable.

In view of the above, it can scarcely admit of doubt that the color and stability of halogen compounds are correlated properties, and probably traceable to the same cause, and therefore this question has suggested itself, Is there not some connection between the color of halogen compounds and their dissociation in the solid state? The facts enumerated above certainly seem to point to such a conclusion. Further, if the color of halogen compounds is in reality due to dissociation, then it follows that the color of any particular halogen compound ought to become deeper and more pronounced on heating; and such has been found to be the case. Lead iodide, mercuric bromiodide, silver iodide, silver bromide, iodoform, tribromphenol bromide, and benzenedibromsulphonamide all become more strongly and highly colored even under boiling water.

The effect of still higher temperatures on the color of some of these compounds has also been tried. All the substances experimented with were heated in small hard glass test-tubes.

Silver Bromide.—When silver bromide is heated it darkens to an orange color even while in the solid state. On still further heating it melts to a deep-red liquid of very much the same appearance as a solution of bromine.

Silver Iodide.—When this compound is heated it changes from yellow to orange and finally to a dark purplish-brown powder. It then melts to a deep reddish-brown liquid which closely resembles iodine in concentrated solutions of potassium iodide, or in the molten state. It is so dark in color as to be opaque except in thin layers, and it is decidedly darker in color than silver bromide in the molten state just as it is at ordinary temperatures. In cooling from the molten state it passes through a strikingly beautiful scarlet tint which is altogether similar to the red modification of mercuric iodide. At still lower temperatures it closely resembles a certain color displayed by molten sulphur.

Lead Bromide.—Lead bromide becomes light yellow when heated and then melts to a liquid which in color resembles sulphur in its first molten stages. This liquid becomes steadily darker as the heating is continued, and finally takes on a deep reddish-brown color which closely resembles that of a solution

of bromine and iodine ; and by continued and prolonged heating bromine is evolved. On cooling, lead bromide passes through the same changes of color in reverse order, and is finally obtained as a white substance again.

Lead Iodide.—This compound steadily darkens in color on being heated, passing through deepening shades of orange up to brownish-crimson of great depth of color. It then melts to a dark brownish-red solution which strongly suggests the color of bromine or iodine ; and at the same time vapors of iodine make their appearance in the tube.

Mercuric Bromiodide, HgBrI.—This compound has a pale yellow color in the cold. On being heated it becomes darker yellow, then orange, and finally melts to a reddish liquid, resembling a solution of bromine or molten sulphur in some of its phases. This compound has been found to sublime unchanged if the heating is continued.

Mercuric Iodide, HgI_2.—The conduct of this compound when heated is of special interest in this connection. When the red variety of this substance is heated, it seems to get darker in color up to a certain point, taking on a reddish-brown tint, which is not observable in the cold, and then very suddenly it changes to the yellow modification. In this connection it is interesting to note that the color of the yellow variety of mercuric iodide is deeper yellow, even in the cold, than that of the bromiodide. On heating the yellow modification of mercuric iodide it becomes darker, and then melts to a light-reddish liquid ; this rapidly increases in depth of color as the heat is applied until it becomes dark port-wine red, like solutions of iodine in potassium iodide ; and at high temperatures in the liquid condition it is difficult to distinguish mercuric iodide from liquid bromine, so far as color and opacity are concerned. It should be observed in this connection that at corresponding temperatures mercuric iodide is always of a deeper and darker tint than the bromiodide, and the same is also true of the other iodides and bromides examined.

Cadmium Iodide.—One modification of this compound exists in the form of beautiful, white scales. When this modification of the compound is heated in a tube it becomes light yel-

low in color, and then melts to a clear reddish-brown liquid, which becomes darker in color and more opaque, the higher it is heated, and finally vapors of iodine appear in the tube.

What is the significance of these results? Is it not that the dissociation begun in the compound in the solid state[1] at the lower temperature simply becomes augmented with the rise of temperature, thereby increasing the color? It is certainly a well-established truth that such is the effect of heat on the dissociation process wherever it has been observed. And if the color of halogen compounds is in reality due to their dissociation in the solid state, then their conduct on heating is just such as would be demanded by the theory. In fact the only break in the continuity of the process, observable on heating the above-named compounds, is the change from the crystalline to the liquid condition and vice-versa.[2] So far as the accompanying change of color is concerned it is gradual and has been found to be essentially the same in variation of tint as is observed in passing through certain aqueous solutions of bromine and iodine of various dilutions.

Let us consider the conduct of lead iodide specifically in the light of this hypothesis. In the liquid state at high temperatures this compound exactly resembles a concentrated solution of potassium periodide. Now it is generally conceded that potassium periodide is largely dissociated in aqueous solutions, and that its color is due to the iodine resulting from this dissociation, and it is further certain that the one molecule of the iodine it contains conducts itself chemically as though it

[1] Richards, in a recent communication on "The Cause of the Retention and Release of Gases Occluded by the Oxides of Metals," has found it necessary to assume that copper oxide is slightly dissociated at red heat; and that auric oxide and silver oxide probably dissociate at comparatively low temperatures. This JOURNAL, **20**, 701.

[2] It is not intended to confuse the dissociation of halogen compounds here under discussion with the electrolytic dissociation of salts, but it is interesting to note that according to LeBlanc, "Many salts possess not inconsiderable conductivities below their melting-points as well as above," Electro-Chemistry, pp. 119–120; and that according to Graetz, "No sudden change in the conductivity of a salt or of its temperature coefficient, is observable at its melting-point" [Wiedemann's Ann., **40**, 18, (1890)]. "From this it must, apparently, be concluded," according to Nernst, "that there is no marked change either in ion friction, or in the electrolytic dissociation, in the liquefaction of a salt" (Theoretical Chemistry, Translation, p. 593). So also on heating halogen compounds, as will be seen in the above, no sudden or marked changes of color are observable, but simply a gradual increase in the depth of tint.

were in the free condition. Therefore, if the color of liquid lead iodide at high temperatures is similar to that of potassium periodide, would not the assumption be justifiable, that this compound is also dissociated at these temperatures. Further, on cooling lead iodide, no sudden break or variation in the color is observable, but it passes by insensible gradations through varying shades of reddish-brown, brownish-crimson, reddish-orange, orange, to yellow; and all of these tints can be imitated by solutions of the element iodine in potassium iodide. Therefore, is it not logical to conclude that the dissociation of lead iodide in the liquid state falls off by insensible gradations until a minimum, but still appreciable, amount is reached in the cold solid? Such certainly would seem to be the case.

Then again, as is well known, lead bromide and lead iodide have nothing in common in color in the solid state, the bromide being pure white, and the iodide yellow. When heated, however, the bromide becomes yellow; the color gradually increases in intensity the more strongly the substance is heated. In other words, by the action of heat it can be made to resemble the iodide in color. In fact, the more strongly these two compounds are heated the more closely do they resemble each other. On the supposition that the color of lead bromide is constitutive, that is, that it is peculiar to the molecule $PbBr_2$ as such, we have no satisfactory explanation of its changes of color on heating, and there is no reason for its showing a resemblance in color to lead iodide at high temperatures. On the supposition that the color of the halogen compounds is due to dissociation, however, we have a satisfactory explanation of these phenomena. In the solid state lead bromide is not dissociated at all, whereas the iodide is to some extent; hence, the former is white while the latter is yellow. As the lead bromide is heated, however, it begins to dissociate, and hence exhibits a yellow color at once. As the temperature is raised, this dissociation increases in amount, and the melted compound looks more and more like lead iodide in the molten state. Furthermore, according to these suppositions, lead bromide, if it changes in color at all, must take on a color resembling that of the iodide, in consequence

of the fact that bromine and iodine themselves closely resemble each other in color, at least under some conditions. This also has been found to be true. In other words, all changes in the color of halogen compounds partake of the nature of additive properties in general, and hence must receive a similar explanation.

There is one other point in this connection which deserves mention, and that has reference to the extent of the dissociation occurring in colored halides in the solid state. At the present stage of our knowledge it is entirely impossible to measure this with any degree of certainty. It should be said, however, in this connection, that the amount of this dissociation must be extremely small. By reference to the foot-note on page 405 it will be seen that 0.000066045 gram of iodine serves to impart a decided yellow color to 20 cc. of a solution of potassium iodide containing 150 grams of potassium iodide in 250 cc. of solution, and having a specific gravity of 1.41; so that this extremely small amount of iodine serves to color at least 28 grams of substance a decided yellow. This corresponds to about 66 parts of iodine in 28 million parts of substance, or to nearly 2.4 parts of iodine per million. If, therefore, only this extremely small amount is necessary to impart a decided yellow color to such a solution, it would seem reasonably certain that the amount of this element necessary to impart such a color as is usually observable in its colored compounds must also be extremely small; and, therefore, that the degree of dissociation of such compounds is also extremely small—so small in fact that it could not be measured except by some colorimetric method.

In conclusion, it must be admitted that the halogens impart a characteristic color to a large number of their compounds. According to Bernthsen[1] "most organic compounds are colorless." "Compounds containing iodine, however, are frequently yellow or red." This characteristic color must be either an additive or a constitutive property. Either the color must be due to the influence exerted by the halogen as a component part of the molecule on the molecule as a whole, *i. e.*, it must be a constitutive property, or the color must be

[1] Organic Chemistry, Eng. Ed., p. 31.

due to the dissociation of a small number of the molecules of the substance whereby a very small amount of the halogen becomes free and assumes its own color, and thereby imparts its characteristic tint to the compound as a whole. On the former assumption it would certainly prove a difficult task to account for the fact that hydriodic acid, containing 99.2 per cent of iodine, is colorless, whereas a great many periodides containing less than 50 per cent of iodine are so highly colored as to resemble the element iodine itself. On the latter assumption, however, this would simply mean that the affinity of hydrogen for iodine is such as to render the dissociation of hydriodic acid impossible at ordinary temperatures; hence the compound is colorless. On the other hand, as is well known, the periodides as a class are very unstable, and hence are strongly colored in consequence of considerable dissociation, even in the solid state. It is therefore believed that the hypothesis under discussion has much to recommend it on the score of simplicity, and that it derives support from a great number of facts; and should it prove to be correct, it would considerably enlarge our physical and chemical conceptions of the solid state.

Mr. A. S. Loevenhart has been of great assistance to me in the preparation of this article, and I desire to thank him in this connection.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, KY., Feb., 1899.

Contributions from the Sheffield Laboratory of Yale University.

LXX.—ON THE FORMATION OF POTASSIUM β-FERRICYANIDE THROUGH THE ACTION OF ACIDS UPON THE NORMAL FERRICYANIDE.

BY JAMES LOCKE AND GASTON H. EDWARDS.

We have shown in a previous paper[1] that when a solution of potassium ferricyanide is heated for a short time with potassium chlorate and hydrochloric acid, an isomer of this salt is obtained, which crystallizes with one molecule of water. This salt had already been obtained by Skraup[2] and others,

[1] This JOURNAL, **21**, 193. [2] Ann. Chem. (Liebig), **189**, 368.

in an impure state, by the action of oxidizing agents, and was regarded by them as an oxidation-product of the normal ferricyanide, with the formula $K_3Fe(CN)_6$. At the time of our first investigation, we likewise ascribed its formation to the oxidizing action of the potassium chlorate, but have since found that it is due to the hydrochloric acid alone, and is, in fact, formed more or less readily by the action of any acid on potassium ferricyanide. Its preparation by former experimenters can thus be readily explained, as their operations were all carried on in acid solutions.

In our first experiments to investigate this point we used the same quantity of hydrochloric acid as in the preparation of the salt with potassium chlorate, that is, the amount required according to the equation given by Skraup,

$$6K_3Fe(CN)_6 + KClO_3 + 6HCl = 6K_2Fe(CN)_6 + 7KCl + 3H_2O,$$

and otherwise performed the experiments exactly as described in our previous article. 50 grams of potassium ferricyanide were dissolved in 100 cc. of water, heated to boiling, and 18 cc. of concentrated hydrochloric acid (sp. gr. 1.19), diluted with three times their volume of water, were added, and the mixture allowed to stand on the water-bath. Small portions were taken out at short intervals, cooled, precipitated with equal volumes of 95 per cent alcohol, and the precipitates filtered off. These various preparations were then tested with bismuth nitrate, with which the α-ferricyanide gives a yellow precipitate, and the β-ferricyanide none. Subsequently, the percentages of cyanogen which they contained were determined by reduction with sodium amalgam, and titration to potassium α-ferricyanide with potassium permanganate.[1]

Two samples of the solution, taken out after the reaction had proceeded one and one-half minutes and three minutes, respectively, gave with alcohol yellow and yellowish-green precipitates, the colors of which were due to the presence of unchanged α-ferricyanide. These showed, with bismuth nitrate, the test characteristic of the latter. At the end of five minutes the originally reddish-yellow solution had assumed the peculiar red-violet color of the β-salt, and the precipitated

[1] This JOURNAL, **21**, 193.

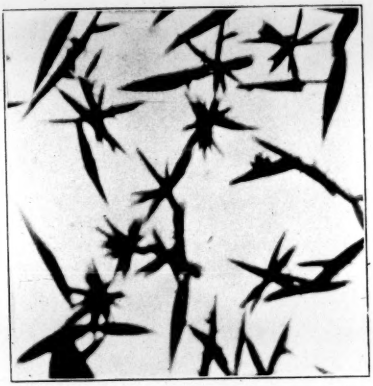


FIG. I.—Potassium β-ferricyanide.

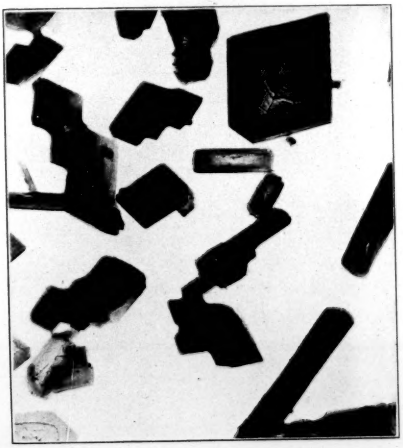


FIG. II.—Potassium α-ferricyanide.

samples then consisted of a completely homogeneous mass of well-formed, olive-green crystals. These showed all the properties of potassium β-ferricyanide, $K_3Fe(CN)_6.H_2O$, as previously described by us. They are most readily recognized by their very characteristic crystal-habit showing the forms illustrated in Fig. I. This is taken from a photomicrograph, as is also Fig. II, which shows crystals of the normal ferricyanide obtained under similar conditions. At the same time the percentage of cyanogen rapidly fell to a value corresponding closely to that calculated for the β-salt; that is, 44.96 per cent. The sample obtained after the reaction had proceeded for ten minutes was of a greenish-black color, and showed no distinct crystallization, indicating that further decomposition had taken place. In this, and subsequent samples also, the percentage of cyanogen had fallen considerably below the value for the β-compound.

The analytical results of this series of experiments are tabulated below.

Series A.

50 grams $K_3Fe(CN)_6$: 18 cc. conc. HCl.
1 cc. $KMnO_4$ solution = 0.03704 gram $K_3Fe(CN)_6$.

No.	Time. Min.	Color.	Weight of substance taken. Gram.	Cc. $KMnO_4$ used.	Cc. $KMnO_4$ calculated for $K_3Fe(CN)_6.H_2O$.	Cc. $KMnO_4$ calculated for $K_3Fe(CN)_6$.	Cyanogen found.
I	1½	yellow	0.1881	4.9	4.81	5.08	45.74
II	3	yellowish-green	0.2616	6.8	6.7	7.06	45.65
III	5	olive	0.2073	5.3	5.31	5.59	44.89
IV	7½	"	0.2919	7.4	7.47	7.88	44.52
V	10	green-black	0.2376	5.9	6.08	6.42	43.60
VI	15	"	....	...	...	...	....
VII	20	"	0.3014	7.3	7.71	8.17	42.53

Cyanogen calculated for $K_3Fe(CN)_6$, 47.41 per cent.
" " " $K_3Fe(CN)_6.H_2O$, 44.96 per cent.

The question next suggested itself, whether it was necessary to have hydrochloric acid present in definite molecular quantity, as above, or whether its action was not merely one

of catalysis, and caused by the presence even of small quantities. In order to decide this, experiments similar to the above were made, in which one-half, one-fourth, and one-eighth of the amount of the acid there used was employed. It was found, not only, that the β-compound was formed in each case, but that its subsequent decomposition by the acid takes place much more slowly than when the acid is more concentrated. The reactions could, therefore, be much more easily followed in these experiments, as a considerable interval elapsed between the point at which the α-salt disappeared and that at which the β-salt noticeably began to decompose. The results of these experiments are tabulated below:

Series B.

50 grams $K_4Fe(CN)_6$; 9 cc. conc. HCl.

No.	Time. Min.	Color.	Weight of substance taken. Gram.	Cc. $KMnO_4$ used.	Cc. $KMnO_4$ calculated for $K_4Fe(CN)_6.3H_2O$.	Cc. $KMnO_4$ calculated for $K_4Fe(CN)_6$.	Cyanogen found.
I	5	yellowish-green	0.2152	5.6	5.51	5.81	45.74
II	10	olive	0.2222	5.7	5.68	5.9	45.03
III	15	"	0.2233	5.7	5.72	6.03	44.82
IV	20	green-black	0.2155	5.2	5.52	5.82	42.37
V	25	"	0.2393	5.7	6.12	6.49	41.83

Series C.

50 grams $K_4Fe(CN)_6$; 4.5 cc. conc. HCl.

I	2	yellow	0.3535	9.3	9.05	9.54	46.19
II	4	yellowish-green	0.3421	8.9	8.75	9.24	45.68
III	6	olive	0.1901	4.9	4.86	5.13	45.26
IV	8	"	0.2569	6.6	6.57	6.94	45.11
V	10	"	0.2263	5.8	5.79	6.11	45.00
VI	15	"	0.2223	5.7	5.69	5.9	45.03
VII	20	green	0.1994	5.0	5.1	5.38	44.03
VIII	25	green-black	0.3195	8.0	8.18	8.63	44.00
IX	30	"	0.2198	5.5	5.63	5.93	43.94

Series D.

50 grams $K_3Fe(CN)_6$; 2.25 cc. conc. HCl.

No.	Time.	Color.	Weight of substance taken.	Cc. $KMnO_4$ used.	Cc. $KMnO_4$ calculated for $K_3Fe(CN)_6 \cdot H_2O$.	Cc. $KMnO_4$ calculated for $K_3Fe(CN)_6$.	Cyanogen found.
	Min.		Gram.				
I	5	yellow	....	..	...	...	....
II	10	"	0.2256	5.9	5.77	6.06	45.92
III	15	yellowish-green	0.1510	3.9	3.86	4.08	45.02
IV	20	olive	0.2121	5.4	5.43	5.73	44.71
V	25	"	0.2584	6.6	6.61	6.98	44.85
VI	35	"	0.2639	6.7	6.75	7.12	44.57
VII	45	"	0.2113	5.3	5.41	5.7	44.04
VIII	55	green	0.2036	5.0	5.21	5.5	43.12
IX	65	green-black	0.2171	5.4	5.55	5.86	43.67
	Hours.						
X	1½	"	0.1745	4.2	4.46	4.71	42.27
XI	2	"	0.2015	4.9	5.17	5.42	42.70
XII	2½	"	0.2010	4.5	5.14	5.43	39.31

In Series *D* it will be seen that in the first fifteen minutes the percentage of cyanogen fell from the value calculated for the *α*-salt, or 47.41 per cent, to 45.02 per cent, or nearly the value calculated for the *β*-salt, a loss of 2.4 per cent. From this point on, the precipitated samples gave no reactions with bismuth nitrate. During the next twenty minutes the percentage of cyanogen fell only 0.45 per cent, and the fractions taken out in this interval were all thoroughly homogeneous and well crystallized. Beyond this point the decomposition again became more rapid, and the samples obtained were of far less satisfactory appearance than those in numbers III–VI.

In Series *B* and *C* similar results were obtained, but the reactions proceeded much more rapidly. In *C*, for instance, the samples ceased to react with bismuth nitrate in eight minutes, and the *β*-salt was noticeably decomposed at the end of twenty minutes. It must, therefore, be concluded that the velocity of the reaction is directly dependent upon the concentration of the acid.

Similar results were obtained when other acids were substituted for hydrochloric acid. Experiments were instituted

with sulphuric, oxalic, and acetic acids. No quantitative determinations were made, however, as it was found impossible, in the first two cases, to obtain the precipitates free from potassium sulphate and potassium oxalate. But that the reaction proceeded in the same way as when hydrochloric acid was used, was readily recognized by the color of the solution and by the appearance of the precipitates. With oxalic acid the β-salt was formed less readily than with sulphuric acid, though in both cases the conversion of the α-salt into its isomer took place more slowly than it did in hydrochloric acid solution. It would thus appear that the catalytic action of different acids, to which the formation of the β-salt is due, is directly dependent upon the degree to which the acid used undergoes ionization. According to this, an acid such as acetic, which ionizes but slightly, should have only a very slow action. This was found to be the case, for with dilute acetic acid we could obtain no β-salt at all, and a solution of ferricyanide, heated for an hour with the concentrated acid (2 molecules), still gave a slight precipitate with bismuth nitrate.

NEW HAVEN, February, 1899.

Contributions from the Chemical Laboratory of Harvard College.

CXI.—TRINITROPHENYLMALONIC ESTER.[1]

[SECOND PAPER.]

BY C. LORING JACKSON AND J. I. PHINNEY.

The work described in this paper was undertaken with the intention of preparing some derivatives of the trinitrophenylmalonic ester (picrylmalonic ester),

$$C_6H_2(NO_2)_3CH(COOC_2H_5)_2,$$

discovered by C. A. Soch and one of us.[2] It has led to the discovery of a second and more stable form of the trinitrophenylmalonic ester, which melts at 64° instead of 58°, the melting-point of the form at first obtained; and we have also prepared the nitrite of this ester,

$$C_6H_2(NO_2)_3CNO(COOC_2H_5)_2,$$

[1] Presented to the American Academy of Arts and Sciences, October 20, 1898.

[2] This JOURNAL, 18, 133.

melting at 109°, the corresponding trinitrophenyltartronic ester,

$$C_6H_2(NO_2)_3COH(COOC_2H_5)_2,$$

melting at 117°, its acetyl derivative,

$$C_6H_2(NO_2)_3COCOCH_3(COOC_2H_5)_2,$$

which melts at 125°, and the trinitrophenylacetic acid,

$$C_6H_2(NO_2)_3CH_2COOH,$$

melting at 161°.

The Two Modifications of Trinitrophenylmalonic Ester.

The trinitrophenylmalonic ester, as prepared by Soch and one of us,[1] crystallized from alcohol in white, long, rather slender, rectangular plates, or when better developed in thick prisms with blunt ends, often as much as 2 centimeters long. It melted at 58°.[2] When we first took up the work again, we also obtained the trinitrophenylmalonic ester exclusively in this form, and confirmed repeatedly the observations given above on its crystalline form and melting-point. Somewhat later we converted a sample of the trinitrophenylmalonic ester into its very characteristic ammonium salt, and upon acidifying this and recrystallizing the ester thus set free we obtained instead of the rectangular plates four- (or six-) sided plates in which two of the opposite angles were unlike,—one being obtuse and the other acute,—so that the crystals were shaped somewhat like a kite; and not only did the form of these crystals differ in such a marked way from the rectangular plates previously obtained, but they also melted at 64° instead of 58°. During this experiment a solution of the ester from one of our preparations of it was evaporating spontaneously on the desk; the next morning these kite-shaped crystals were deposited from it, although it had previously yielded only the rectangular plates melting at 58°, and since then we have obtained from all our preparations only the form melting at 64°, whereas before exactly similar preparations had given

[1] *Loc. cit.*

[2] In the previous paper this melting-point is given as 59°, but it must be changed to 58°, as it was found after that paper was published that the zero point of the thermometer used had changed.

us exclusively the form melting at 58°, as has already been stated. Varying the conditions of the preparations, such as carrying them on in cooled or warmed solutions, or with longer or shorter standing, did not modify the result, so that we have not succeeded in adding to the stock of the modification melting at 58°, which we had on hand, when we encountered the other form.

The following experiment seems to us to suggest a possible explanation of these results: a solution of the form melting at 58° was evaporated until it began to deposit the rectangular crystals, and then inoculated with a speck of the form melting at 64°, when at once the kite-shaped crystals of this form began to appear, and no more rectangular crystals were produced. This experiment was tried several times early in our work; it could not be repeated later, as then recrystallization alone of the form melting at 58° was enough to convert it partially or even completely into the form melting at 64°. As then a small amount of the form melting at 64° is enough to convert a large quantity of the other form into this, it seems probable that the small amount of the more stable form floating in the air of the laboratory as dust was enough to bring about this change, and to give us this more stable modification as the sole product of our preparations, and even of recrystallizations of the less stable form. The view that the inoculation of the solutions proceeded from the dust in the air is supported by the following observations: A preparation made with new apparatus and fresh material, but in the laboratory where these experiments had been tried, yielded only the stable form melting at 64°. Crystallizations of the form melting at 58° gave, after the work had been in progress some time, the form melting at 64°. We then crystallized a specimen melting at 58° in a fresh room, which had not been used for these experiments, and obtained in this way the rectangular plates melting at 58°; but upon recrystallizing the specimen, the form melting at 64° appeared, and after this the first crystallization of a fresh specimen melting at 58° in this room gave crystals of the form melting at 64°. A probable explanation of these latter observations is that there was a little dust of the more stable modification in this room coming

from the clothes of one of us, who used it as a lecture-room, and that this was sufficient gradually to inoculate the solutions. As the laboratory building, apparently contaminated with the dust of the more stable form, seemed to offer little chance of preparing more of the form melting at 58°, we postponed publishing this paper for some years, in the hope that one of us (who left Cambridge at the end of the year) might prepare more of the form melting at 58° by working in entirely new surroundings. Unfortunately, the pressure of other duties has prevented the carrying out of this work, and we have decided that it is wiser to publish now the results already obtained rather than to postpone the appearance of the paper to a still later date.

The conversion of the form melting at 58° into that melting at 64° has been brought about by us in the following ways: By its conversion into the ammonium salt and setting free the ester by acidification;[1] by inoculating a saturated alcoholic solution with a crystal of the form melting at 64°; by melting the less stable form it was partially changed into that melting at 64°, and, if the melting was repeated, the change became complete. It is possible, however, that this change might have been due to inoculation from dust. On the other hand, we have not succeeded in converting the form melting at 64° into that melting at 58° in spite of many experiments; even melting the more stable form and stirring it with a rod tipped with the modification melting at 58° did not have the desired effect.

The substance melting at 64° was purified by crystallization from alcohol, and after being dried *in vacuo* was analyzed with the following results:

I. 0.2050 gram of the substance gave, on combustion, 0.3149 gram of carbonic dioxide and 0.0736 gram of water.

II. 0.2007 gram of substance gave 0.3078 gram of carbonic dioxide and 0.0789 gram of water.

III. 0.2040 gram of substance gave 20.5 cc. of nitrogen at a temperature of 21° and a pressure of 759.6 mm.

[1] In my earlier work with Soch, the sodium salt yielded, on acidification, the ester melting at 58°.—C. L. J.

	Calculated for $C_6H_3(NO_2)_2CH(COOC_2H_5)_2$.	Found. I.	II.	III.
C	42.05	41.89	41.82	....
H	3.50	3.98	4.36	....
N	11.32	....	....	11.41

The combustion of this substance must be carried on as slowly as possible, as it has a strong tendency to explode.

The molecular weight of the substance was also determined by the method of Raoult with the following results:

I. Weight of benzol used 19.2120 grams. Substance 0.3291 gram. Reduction of freezing-point 0°.230.

II. Weight of benzol used 15.7244 grams. Substance 0.3428 gram. Reduction of freezing-point 0°.306.

III. Weight of benzol used and weight of substance the same as in II. Reduction of freezing-point 0°.297.

	Calculated for $C_6H_3(NO_2)_2CH(COOC_2H_5)_2$.	Found. I.	II.	III.
Molecular weight	371	365.1	349.0	359.6

From these results there can be no doubt that the preparation melting at 64° was trinitrophenylmalonic ester.

It is worth while to point out here that the form melting at 58° could not have owed its peculiarities in melting-point and crystalline form to the presence of a small quantity of some impurity, since it was repeatedly brought to a constant melting-point both by Dr. Soch and by us; and, if this explanation were correct, this form should have been the first product of the preparations in our later work, whereas, after we had once obtained the form melting at 64°, we could not prepare the other. Dr. Soch's analyses of the form melting at 58° also show that it was pure.

	Calculated.	Found.	
N	11.32	11.75	11.38

We are therefore led to the conclusion that the trinitrophenylmalonic ester exists in two isomeric forms.

The isomerism of these two forms is probably due to the same cause as that of the red and yellow anilidotrinitrophenyltartronic esters (melting at 143° and 122°) discovered by W. B. Bentley[1] and one of us. It seems more doubtful whether it is related to the isomerism of the formylphenylacetic esters

[1] This JOURNAL, 14, 348.

discovered by W. Wislicenus,[1] of the dibenzoylacetones[2] and the benzoates of oxymethylenacetone[3] of Claisen, and the benzalanilinacetacetic esters of R. Schiff,[4] since both of our isomers can be dissolved in alkaline solutions without alteration, whereas one of the most marked differences between the isomers in these other cases consists in the fact that one dissolves in alkalies and the other does not.

Our present knowledge of these substances is not sufficient to allow us to make a final statement in regard to the cause of this isomerism, but the following discussion is given for what it is worth. The fact that each form has been converted into a salt, and set free from this unaltered upon acidification, would indicate that it is a case of chemical rather than physical isomerism; and, if this is true, as the symmetrical nature of the substance would forbid stereomeric isomers, the only probable explanation which we have been able to find is that the isomerism depends on differences of structure in the malonic group, as indicated by the following formulas:

I. $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.

II. $C_6H_2(NO_2)_3C\begin{matrix}COOC_2H_5\\ \diagup\\ \diagdown\\ COH.OC_2H_5\end{matrix}$.

In other words, that the isomerism is analogous to that of the bodies studied by W. Wislicenus, Claisen, and R. Schiff. There are, however, objections to this explanation, and, as we have said already, the whole subject needs further investigation before any satisfactory theory can be found.

Properties of the Trinitrophenylmalonic Ester Melting at 64°.—Crystallized from alcohol, it forms white plates, usually bounded by four or six sides. In the four-sided form there are two unlike opposite angles, one obtuse, the other acute, which give a very characteristic appearance to the crystals. The six-sided form is produced by two planes truncating the similar angles in the four-sided form. Both these forms resemble a kite in shape. Occasionally much more complex crystals were observed, having a parallel-sided projection arising from the middle of the obtuse end, and also terminated by

[1] Ber. d. chem. Ges., **28**, 767.
[2] Ann. Chem. (Liebig), **277**, 188.
[3] Ber. d. chem. Ges., **35**, 1785.
[4] *Ibid.*, **31**, 601.

an obtuse angle; this form had a general resemblance to the "spade" in playing cards. The plates were often thick, especially when having the complex form last described. The substance turns yellow on long exposure to the air, and imparts to alcohol a marked crimson color, which also has been observed on the ground-glass stopper of the bottle in which it was kept. In this case the color may have been due, however, to some alkali from the glass, but this was not the case in the alcoholic solution, as the color was only partially discharged by acidification. The modification melting at 58° forms similar crimson solutions. It melts at 64° to a red liquid. Its solubility in the organic solvents is essentially the same as that of the form melting at 58°; that is, it is very soluble in chloroform, ether, benzol, or glacial acetic acid; somewhat less so in carbonic disulphide; soluble in cold alcohol, freely in hot, rather more soluble in methyl than in ethyl alcohol; insoluble in ligroin, or cold water, slightly soluble in hot water.

The action of acids upon this more stable trinitrophenylmalonic ester is described in some of the following paragraphs of this paper. Alkalies give with it dark-red salts, which crystallize well. The ammonium salt is especially characteristic; it was made by adding an excess of aqueous ammonic hydrate to a warm, nearly saturated, alcoholic solution of the trinitrophenylmalonic ester. The solution took on a deep purplish-red color, and in a few seconds the whole solidified to a thick semisolid mass having the purplish-red color and consistency of clotted blood. A microscopic examination showed that this mass was made up of long, very slender, hair-like crystals, which, after drying, had a rich golden-brown color and a silky luster. The salt decomposed below 100°, at first turning black, but afterward melting to a clear, yellowish liquid, which exploded at higher temperatures. It is rather sparingly soluble in water, soluble in alcohol, chloroform, or acetone, insoluble in ligroin. The solutions have a dark-red color, but if the solution in water or alcohol is boiled for some time it turns yellowish-brown; unfortunately no product could be obtained from such solutions in a state fit for analysis.

An aqueous solution of the ammonium salt gave the following characteristic precipitates:

With salts of *barium* an abundant, crystalline, amethystine precipitate.

With salts of *strontium* a dark-red precipitate.

With salts of *calcium* a brick-red precipitate.

With salts of *zinc* an abundant, crystalline, scarlet precipitate, turning to reddish-brown on standing.

With salts of *cadmium* a granular, scarlet precipitate.

With salts of *copper* a heavy, flaky precipitate, varying from reddish-yellow to brownish-red.

With salts of *lead* heavy, dark-red flocks.

Salts of the other metals gave precipitates as a general rule, but they were not characteristic. The behavior with argentic nitrate, however, should be especially mentioned, as this gave no precipitate in dilute solutions, and only a slight, cloudy, dark-red one when the solutions were strong. The barium, zinc, and copper salts were analyzed.

Barium Salt.—This salt was made by adding a solution of baric chloride to the aqueous solution of the ammonium salt. The heavy purple flocks thus obtained were washed with water, dried at 100°, and analyzed with the following result:

0.4864 gram of the salt gave 0.1236 gram of baric sulphate.

	Calculated for $[C_6H_2(NO_2)_3C(COOC_2H_5)_2]_2Ba$.	Found.
Ba	15.62	14.95

The salt is so hygroscopic that 0.2 gram will gain as much as 4 milligrams during the time of weighing, if it is in an open watch-glass. In evaporating it with sulphuric acid for analysis, care must be taken not to apply the heat too suddenly at first, or an explosion may result. The best plan is to heat the mixture for some time to 100°, as then the decomposition goes on quietly.

Properties.—The barium salt appears as a purple, obscurely crystalline mass, essentially insoluble in water. It explodes if heated to 120°.

Zinc Salt.—This salt was made by mixing solutions of zincic sulphate and the ammonium salt of the ester. It was purified by washing, dried at 100°, and analyzed with the following result:

0.4869 gram of the salt gave 0.0478 gram of zincic oxide.

	Calculated for $[C_6H_2(NO_2)_3C(COOC_2H_5)_2]_2Zn$	Found.
Zn	8.07	7.88

Properties.—The zinc salt forms a reddish-prown crystalline mass, essentially insoluble in water, but very hygroscopic. Like the barium salt it explodes easily, if heated with strong sulphuric acid, and therefore the same precautions must be used in analyzing it which were recommended in the case of the barium salt.

Copper Salt.—This salt was made by mixing aqueous solutions of cupric sulphate and the ammonium salt of the ester. It was purified by washing with water, and after drying at 100° gave the following result on analysis :

0.3012 gram of the salt gave 0.0291 gram of cupric oxide.

	Calculated for $[C_6H_2(NO_2)_3C(COOC_2H_5)_2]_2Cu.$	Found.
Cu	7.92	7.72

Properties.—The copper salt is a brownish-red powder, essentially insoluble in water. It resembles the barium and zinc salt in being very hygroscopic, and exploding easily, when heated with strong sulphuric acid.

Action of Nitric Acid on Trinitrophenylmalonic Ester.

The action of nitric acid upon this substance is similar to its action with the bromtrinitrophenylmalonic ester,[1] that is, the nitrite or the substituted tartronic ester is obtained according to the length of the treatment.

Nitrite of Trinitrophenylmalonic Ester,
$C_6H_2(NO_2)_3CONO(COOC_2H_5)_2$.

Two grams of the trinitrophenylmalonic ester were heated on the steam-bath with about 15 cc. of common strong nitric acid. After three minutes the ester had melted to a clear, red, oily globule, and the entire liquid had taken on a reddish color. If the process was continued for two minutes more, the globule went into solution. The heating should not be continued beyond this point; in fact, it can be stopped to advantage even as soon as the globule of the melted substance is

[1] This JOURNAL, 14, 336, 345.

formed. If all the organic matter had gone into solution, reddish crystals separated in large quantity, as the liquid cooled. These were purified by washing with water and several crystallizations from alcohol until they showed the constant melting-point 109°. The globule, if the process was stopped before it disappeared, was allowed to solidify, and then purified in the same way. The substance was dried *in vacuo* and analyzed with the following result:

0.2190 gram of the substance gave 25.8 cc. of nitrogen, at a temperature of 20° and a pressure of 760.8 mm.

	Calculated for $C_6H_3(NO_2)_2CNO_2(COOC_2H_5)_2$.	Found.
N	13.46	13.46

Properties of the Nitrite of Trinitrophenylmalonic Ester.

It crystallizes in long, flat, white prisms, apparently belonging to the monoclinic system, usually terminated by two planes at an obtuse angle to each other, but sometimes only by a single plane. It melts at 109° with decomposition, as shown by the appearance of a red color. It is easily soluble in ethyl or methyl alcohol, or in chloroform, ether, benzol, glacial acetic acid, or acetone; nearly insoluble in carbonic disulphide; essentially insoluble in water, when cold, very slightly soluble in hot water, giving a pink solution. The three strong acids have no apparent action with it in the cold; strong sulphuric acid, when hot, decomposes it, as shown by the dark color produced and the evolution of gas; strong nitric acid, when hot, converts it into the corresponding tartronic ester. Alkalies have no action upon it at first, but gradually decompose it in the cold with the formation of a red solution. This action is much hastened by heat, but we have made no attempt to isolate the uninviting product.

In all these respects the nitrite of trinitrophenylmalonic ester resembles the nitrite of bromtrinitrophenylmalonic ester,[1] but we have not succeeded in converting the former into the corresponding tartronic ester by decomposition by heat, as was done with the latter. No crystalline substance could be obtained from the viscous red product of the fusion.

[1] This JOURNAL, 14, 339.

Trinitrophenyltartronic Ester, $C_6H_3(NO_2)_2COH(COOC_2H_5)_2$.

This substance was obtained by long continued action of hot nitric acid on trinitrophenylmalonic ester, or by the action of the same reagent on the nitrite just described. Two grams of trinitrophenylmalonic ester were warmed in a porcelain dish on the water-bath with about 15 cc. of common strong nitric acid, more acid being added from time to time to take the place of that which evaporated. To secure the complete formation of the tartronic ester, the heating should be continued for five hours. If the acid solution was not too concentrated, it deposited on cooling long needles of a pink color arranged in rosettes. Stronger solutions gave a more or less red solid cake of the same compound. It was purified by washing with water, and two recrystallizations from alcohol by cooling, when it showed the constant melting-point 117°, and after drying *in vacuo* was analyzed with the following results:

I. 0.2129 gram of the substance gave 20.8 cc. of nitrogen at a temperature of 21° and a pressure of 769.7 mm.

II. 0.2051 gram gave 20.3 cc. of nitrogen at a temperature of 25° and a pressure of 750.3 mm.

	Calculated for $C_6H_3(NO_2)_2COH(COOC_2H_5)_2$.	Found. I.	Found. II.
N	10.85	11.24	10.87

The analysis of this substance gave much trouble, because of the ease with which it exploded, but the difficulties were overcome by mixing it with a large amount of cupric oxide, and heating very carefully.

Properties of Trinitrophenyltartronic Ester.—It forms white, fluffy needles in clusters like sheaves or even circles. Under the microscope the crystals are seen to be slender prisms terminated by a single plane at an oblique angle. Its melting-point is 117°. It is easily soluble in ethyl or methyl alcohol, in fact the hot concentrated solution in ethyl alcohol is so strong that it solidifies nearly completely on cooling. It is also easily soluble in ether, benzol, chloroform, or acetone; soluble in glacial acetic acid; somewhat soluble in carbonic disulphide; soluble with difficulty in ligroin; insoluble in cold water, slightly soluble with decomposition in hot, forming a reddish solution. The three strong acids have no apparent effect

on it in the cold, but hot strong sulphuric acid decomposes it, giving a dark color and an evolution of gas. Alkalies give with it at once dark, blood-red solutions probably containing its salts, but these decompose rapidly, turning dirty-brown, and we have not succeeded in isolating the salts themselves, or any definite compounds from their decomposition-products.

Trinitrophenylacetyltartronic Ester,

$C_6H_2(NO_2)_3C(OCOCH_3)(COOC_2H_5)_2$.

Acetyl chloride dissolves trinitrophenyltartronic ester easily, but does not react with it either at ordinary temperatures, or when heated on the steam-bath in open vessels. We accordingly proceeded as follows: Three grams of trinitrophenyltartronic ester were heated with 15 to 20 cc. of acetyl chloride in a sealed tube to 110° for five or six hours. Care was taken that the temperature did not go too high, as at 140° a blackish decomposition-product was also formed, which made the purification of the product more difficult. On evaporating off the excess of acetyl chloride white crystals separated, which were purified by crystallization from alcohol until they showed the constant melting-point 125°, when they were dried *in vacuo*, and analyzed with the following result:

0.2201 gram of the substance gave 19.4 cc. of nitrogen at a temperature of 24° and a pressure of 761.6 mm.

	Calculated for $C_6H_2(NO_2)_3COC_2H_2O(COOC_2H_5)_2$.	Found.
N	9.79	9.88

Properties of Trinitrophenylacetyltartronic Ester.—It forms white, flat, rather broad prisms, or perhaps they should be called tables, terminated by two planes, and apparently belonging to the monoclinic system. It melts at 125°, and is easily soluble in ethyl or methyl alcohol, benzol, chloroform, or acetone; somewhat soluble in ether, less so in carbonic disulphide; soluble in glacial acetic acid; insoluble in ligroin; insoluble in cold water, slightly soluble in hot, forming a pink solution. Strong hydrochloric acid does not dissolve it. Nitric acid when hot dissolves it apparently without decomposition. Sulphuric acid dissolves it, and decomposes it, when heated. Alkalies have no effect on it in the cold, but,

if heated with it, form the red salts of its decomposition-product.

The benzoyl derivative of trinitrophenyltartronic ester was also made, but the close of the academic year prevented us from getting a satisfactory analysis of it. It was made by heating the tartronic ester with benzoyl chloride in a sealed tube to 110° for four or five hours. On evaporating off the excess of benzoyl chloride it was obtained in white crystals, which were purified by recrystallization from alcohol until they showed the constant melting-point 152°.

Saponification of Trinitrophenylmalonic Ester.

In all these experiments the modification melting at 64° was used. The method of saponification adopted was that which had given such excellent results with the other substituted malonic esters studied in this laboratory, that is, the action of sulphuric acid diluted to a specific gravity of 1.44. Five grams of trinitrophenylmalonic ester were mixed with 100 cc. of this acid, and the mixture boiled in a flask with a return-condenser. The ester melted almost immediately to a straw-colored oily liquid, which gradually decomposed with evolution of gas, and finally was completely dissolved. This usually took place in from one and a half to two and a half hours, and showed that the reaction had come to an end. During the earlier part of the boiling the liquid appearing in the condenser had a pinkish color, but this disappeared later in the process. As soon as all the ester had dissolved, the liquid was allowed to cool, when it deposited a bulky precipitate made up of yellowish-white needles. This substance consisted of the trinitrophenylacetic acid, and was purified in the way described in the following paragraph.

Trinitrophenylacetic Acid, $C_6H_2(NO_2)_3CH_2COOH$.—The purification of this substance cannot be effected by crystallization from alcohol or water, as either of these solvents converts it into the corresponding substituted toluol,

$$C_6H_2(NO_2)_3CH_3.$$

We tried at first as a solvent water containing a small amount of sulphuric acid, since this had given excellent results with

bromdinitrophenylacetic acid;[1] but, whereas with that substance a few drops of sulphuric acid were sufficient to prevent the formation of the substituted toluol, we found that even 1 per cent of acid did not produce this effect with the trinitrophenylacetic acid, and that the amount must be raised to 5 per cent to insure perfect safety. Fortunately it was not necessary to use this rather strongly acidified water, as benzol proved to be an excellent solvent for the substance. Accordingly the crystals, which formed the product of the saponification (see the preceding section), were filtered from the sulphuric acid through glass wool, washed with water, dried, and recrystallized from benzol until they showed the constant melting-point 161°, when they were dried at 100° and analyzed with the following results:

I. 0.2020 gram of the substance gave 28.2 cc. of nitrogen at a temperature of 22° and a pressure of 750.8 mm.

II. 0.2093 gram of the substance gave 28.4 cc. of nitrogen at a temperature of 20° and a pressure of 758.3 mm.

	Calculated for $C_6H_2(NO_2)_3CH_2COOH$.	Found. I.	II.
N	15.50	15.59	15.46

Properties of Trinitrophenylacetic Acid.—It crystallizes from benzol in short needles arranged in sheaf-shaped bunches, and melts at 161°. As at first prepared it is white, but it turns pink on standing, even when in a corked tube, and this change is due to decomposition, as it is accompanied by an alteration in the melting-point. It dissolves in ethyl or methyl alcohol with a pink color, but this solution produces a decomposition, the trinitrophenylacetic acid losing carbonic dioxide and forming trinitrotoluol, which is left in a nearly pure state on the evaporation of the solvent. It was recognized by its melting-point, 81°. Willbrand[2] gives 82°, Mills[3] 78°.84 and 80°.52. (It is possible that further crystallization might have raised the melting-point of our specimen to 82°.) The trinitrophenylacetic acid, therefore, is less stable than the bromdinitrophenylacetic acid, as two evaporations with alcohol were necessary to convert this entirely into the corresponding

[1] This JOURNAL, **11**, 552. [2] Ann. Chem. (Liebig), **127**, 178.
[3] Phil. Mag. [5], **14**, 27.

bromdinitrotoluol. One crystallization of the trinitrophenylacetic acid from boiling water was sufficient also to form the trinitrotoluol, and, as has been already said, the addition of 5 per cent. of sulphuric acid was necessary to prevent this action. The aqueous solution had a pink color like that of the alcoholic solution, but we have not succeeded in discovering the cause of this coloration, which disappears from the solutions, as the substituted toluol is purified by recrystallization. The solvents which follow dissolve the trinitrophenylacetic acid without decomposition; easily soluble in ether, glacial acetic acid, acetone, or ligroin; soluble in chloroform, less so in benzol or carbonic disulphide. The best solvent for it is benzol. The three strong acids seem to dissolve it without decomposition; it is more soluble in nitric acid or sulphuric acid than in hydrochloric acid. Alkalies dissolve it easily, forming deep blood-red solutions of its salts, but we have not yet succeeded in bringing any of these salts into a state fit for analysis.

Attempts to Make Ditrinitrophenylmalonic Ester.

Dittrich,[1] in his work on the action of picryl chloride on sodium acetacetic ester, obtained without difficulty a ditrinitrophenylacetacetic ester; in fact this substance occurred as a secondary product in his preparations of trinitrophenylacetacetic ester, when he used the reagents in molecular proportions. It seems strange, therefore, that we have never observed the formation of a ditrinitrophenylmalonic ester as a secondary product in any of our preparations of the monosubstituted ester. In the hope of preparing this substance (ditrinitrophenylmalonic ester) we converted 5 grams of the trinitrophenylmalonic ester into its sodium salt by treatment with the sodic ethylate from 0.31 gram of sodium, and then treated it with 3.4 grams of picryl chloride. The mixture was allowed to stand at ordinary temperatures over night, and, as no apparent change had taken place, it was divided into two portions, one of which was heated on the steam-bath until it turned brown, and the other allowed to stand two weeks, when it had also turned brown, and deposited crystals of sodic

[1] Ber. d. chem. Ges., **23**, 2720.

chloride. The brown solutions, whether obtained by heating or by standing, yielded sodic picrate and a brown viscous mass, from which nothing fit for analysis could be isolated. A repetition of the experiment under other conditions gave the same result. It seems, therefore, that picryl chloride brings about a deep-seated decomposition when it acts on the sodium salt of the trinitrophenylmalonic ester, as the ditrinitrophenylmalonic ester would be without doubt a well-crystallized compound. The products of this reaction recall Dittrich's description of the substances obtained by him from the action of picryl chloride on sodium malonic ester (pikrinsaures Natrium neben schmierigen Zersetzungsproducten des Malonsäureesters), and it may be that the presence of an excess of picryl chloride was the cause of his failure to obtain trinitrophenylmalonic ester, although this does not appear from the statement in his paper.

Some experiments on the action of aniline on trinitrophenylbrommalonic ester yielded only viscous unmanageable products; and boiling it with water gave no more promising results.

We have also tried several times to detect the presence of trinitrobenzol in the secondary products of the action of sodium malonic ester on picryl chloride, but without success. It seems, therefore, that the replacement of the chlorine of the picryl chloride by hydrogen does not take place under these conditions to any great extent, if it occurs at all.

Contributions from the Chemical Laboratory, University of Oregon.

I.—THE RELATION OF TRIVALENT TO PENTAVALENT NITROGEN.

By Arthur Lachman.

[FIRST PAPER.]

THE ACTION OF ZINC ETHYL ON NITRO- AND NITROSO-COMPOUNDS.

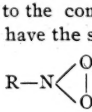
Under the above general title it is proposed to publish, from time to time, a series of more or less connected experimental investigations, their common feature being a study of the

changes of valence of nitrogen atoms. The present paper deals with the structure of the nitro-group, $-NO_2$.

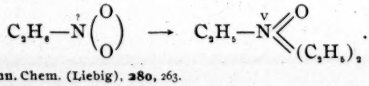
In one form or another, the problem raised by this simple atonic grouping is attracting considerable attention. Without entering into detail, two conditions of the subject may be selected from the great mass of material. In the first place, experimental work has dealt almost wholly with the structure of acidic-nitro compounds and their salts, nitroparaffin salts,[1] isomeric nitroparaffins of the benzyl series,[2] primary nitramines,[3] isonitramines,[4] and primary nitrosamines.[5] These substances are not treated in the present paper, and this brief reference will suffice. In the second place, the structure of the neutral nitro-group is regarded as entirely unsettled,[6] and no experiments have been made to unravel it.

In fact, what little evidence can be adduced in support of one or the other possible formulæ,

is wholly deductive in its character. Spectrochemical calculations have led Brühl[6] to the conclusion that nitroparaffins as well as nitrobenzenes have the same structure ; *viz.*,

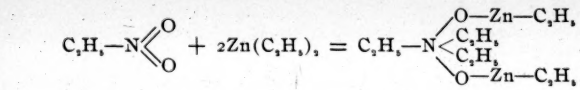


The same charge of deductive reasoning may be made against the single experimental research dealing with our problem. Bewad,[7] in an attempt to ascertain the structure of nitroethane, found that this substance reacts with zinc ethyl, producing triethylamine oxide. This reaction may be regarded as the replacement of an oxygen atom in nitroethane by its equivalent, two ethyl groups :

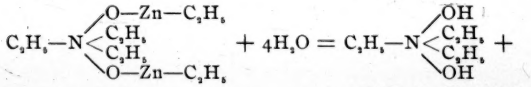


[1] Nef : Ann. Chem. (Liebig), **280**, 263.
[2] Hantzsch: Ber. d. chem. Ges., **29**, 699, 2251.
[3] Thiele and Lachman : Ann. Chem. (Liebig), **288**, 271, 280.
[4] Traube : Ber. d. chem. Ges., **28**, 2297.
[5] Cf. Meyer-Jacobson, Lehrbuch, p. 254.
[6] Ber. d. chem. Ges., **31**, 1350.
[7] *Ibid.*, (Ref.), **21**, 479 ; **22**, 250.

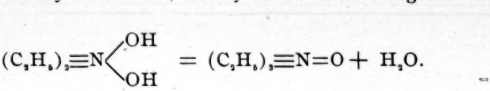
Assuming that zinc ethyl acts on nitrogen-oxygen compounds as it does on the carbonyl group, Bewad interpreted the mechanism of this reaction as follows: In the first place addition of two molecules of zinc ethyl occurs :



Reacting with water in the usual manner, this addition-product forms dihydroxytriethylamine :

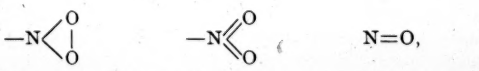


which finally loses water, triethylamine oxide being the result :



For lack of other evidence, the interpretation seems plausible enough. It is strange, however, that Bewad recommends the use of but one molecule of zinc ethyl ; the employment of two led him to an entirely different substance, whose constitution he did not determine.

The question which Bewad's interpretation raises, however, suggests a possible mode of approach. If we compare the two structures under question with the constitution of the nitroso-group,



we see that a doubly linked oxygen atom occurs in the latter and in one of the former. If, therefore, the nitro-group contains oxygen atoms in this form, we may reasonably expect to find nitroso-reactions duplicated, to a greater or less extent, in the corresponding reactions of nitro-compounds. Conversely, marked differences in such reactions would lead us to the opposite conclusion.

From this point of view, various nitroso- and nitro-compounds have been subjected to the action of zinc ethyl. Two prefatory explanations are in order. In the first place, but one representative of the numerous subgroups has been examined. This limitation was imposed by the few facilities at my command, and by the necessity of a general, though incomplete, survey of the field as a whole. In the second place, the results here recorded apply only to a laboratory temperature whose average is 10°, and whose maximum does not exceed 15°. On warming the various substances with zinc ethyl, the reactions assume a complicated character which greatly increases the difficulties of the work, and above all renders comparisons impossible. The results of the reactions at higher temperatures are interesting in themselves, however, and they will be reported at some later date.

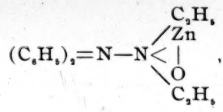
Theoretical Part.

Three nitrosamines were examined. Diethylnitrosamine, $(C_2H_5)_2N—NO$, purely aliphatic, and phenylmethylnitrosamine, $\begin{matrix} CH_3 \\ C_6H_5 \end{matrix}\!\!>\!N—NO$, semiaromatic, do not react with zinc ethyl. Diphenylnitrosamine, $(C_6H_5)_2N—NO$, reacts with violence, so that the substances must be brought together in dilute solution. We may reasonably conclude that increasing negativity of the molecule as a whole enables the nitroso-group to react with zinc ethyl.

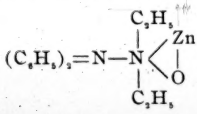
The nature of this reaction is novel and unparalleled. There is formed a well-characterized addition-product, consisting of one molecule each of zinc ethyl and diphenylnitrosamine. This addition-product is decomposed by water, without evolution of gas; the products are zinc hydroxide, diphenylamine, and a volatile base. As the theoretical quantity of diphenylamine is obtained, diphenylnitrosamine reacts completely with zinc ethyl—a condition which has not been observed in the case of any of the other nitrogen compounds investigated. The volatile base at first occasioned much trouble, owing to the impossibility of obtaining it or its salts in a pure state; but as it is a strong reducing-agent, and is converted by reduction into diethylamine, it can be nothing but $\beta\beta$-diethyl-

hydroxylamine.[1] Nearly 50 per cent of the theoretical quantity of diethylamine was isolated.

The constitution of the addition-product is thus fully explained by the following formula:



which satisfactorily accounts for its decomposition by water:



$$+ 2H_2O = (C_6H_5)_2{=}NH +$$

$$(C_6H_5)_2N.OH + Zn(OH)_2.$$

I know of no other instance in which zinc ethyl thus parts with both alkyls at once to a single other atom. If this unexpected reaction is to be explained by the affinity of nitrogen for alkyl, it is inconceivable why the much more basic diethylnitrosamine does not manifest the same activity. If, on the other hand, it is due to the general negativity of the molecule, it is equally strange that nitrosobenzene does not behave similarly (see next paragraph).

Among compounds containing the nitroso-group directly attached to carbon, but one could be investigated. This was nitrosobenzene. The reaction between nitrosobenzene and zinc ethyl is far from simple,[2] and it will be impossible to give any equation representing it. The salient features are the violence of the reaction, which takes place immediately even in dilute solution, with evolution of much heat; the formation of azoxybenzene as chief product, and of phenylhydroxylamine in almost equal quantity; the production of smaller amounts of aniline and ethylaniline; and the total absence of diethylaniline. The formation of azoxybenzene is of course easily accounted for by the interaction of nitrosobenzene with

[1] An attempt will be made to prepare this base in quantity by this curious synthesis.

[2] Cf. with the reaction between nitrosobenzene and diazomethane (Von Pechmann: Ber. d. chem. Ges., **30**, 2461). There are many points of similarity.

phenylhydroxylamine.[1] As to this latter substance, the following equation may be offered (with reservation) :

$$C_6H_5—N\begin{matrix}OC_2H_5\\ZnC_2H_5\end{matrix} + 3H_2O = C_6H_5N\begin{matrix}OH + C_2H_5OH\\H + Zn(OH)_2 + C_2H_6\end{matrix}.$$

No simple equations can be suggested that will explain the appearance of aniline and ethylaniline. A considerable quantity of neutral, black tar is a constant product ; its properties are uninviting, but further investigation of it may lead to a more complete explanation of this complex reaction.

As intermediate between the two groups of compounds just considered, the behavior of azoxybenzene towards zinc ethyl offered an interesting problem. The constitution of this substance is commonly given thus :

$$C_6H_5—N—N—C_6H_5.$$
$$\quad\quad\quad

The resemblance to the latter substance seems the closer, by the fact that diphenylnitrosamine and azoxybenzene are isomeric. A substance with the Brühl formula ought, therefore, to react easily and promptly with zinc ethyl. Experiment showed, however, that azoxybenzene does not react with zinc ethyl even on standing fourteen days. Azoxybenzene thus has the structure usually assigned to it. A further conclusion may be drawn from this result—an oxygen atom linked to two other atoms is not readily attacked by zinc ethyl—a conclusion of value in connection with one of the possible structures of the nitro-group.

Three nitro-compounds were studied—dimethylnitramine, nitroethane, and nitrobenzene. Dimethylnitramine, $(CH_3)_2N—NO_2$, does not react with zinc ethyl. Unfortunately, no binding conclusion can be drawn from this result, since the corresponding nitroso-compound (diethylnitrosamine) exhibits no greater tendency to react. In view of the conclusion reached further on concerning the other two compounds, however, the conjecture may be hazarded that both nitrogen atoms are trivalent:

$$(CH_3)_2\overset{III}{N}—\overset{III}{N}\begin{matrix}O\\ \|\\ O\end{matrix}$$

As regards the conduct of nitroethane, Bewad's[1] results can be almost wholly verified. The amount of triethylamine oxide produced is about 12 per cent of the theoretical yield; no attempt has been made for the present to ascertain the cause of the great loss. At variance with Bewad, however, I found that the presence of two molecules of zinc ethyl does not prevent the appearance of triethylamine oxide; on the contrary, the yield was increased to 25 per cent. The cause of this discrepancy can only be surmised.[2]

Nitrobenzene proves a great surprise, for it reacts but slightly with zinc ethyl. Nearly fifty per cent is recovered unaltered, and the bulk of the reaction-product is a neutral, sticky mass of disagreeable character. The small amount of

[1] *Loc. cit.*

[2] On allowing a mixture of equal molecules of the substances to stand forty-five days, hardly any oxide was obtained. Perhaps Bewad allowed his solution to stand too long.

basic matter obtained consists chiefly of hydroxylamine, with traces of aniline and monoethylaniline; no diethylaniline could be found. Similar results were obtained when two molecules of zinc ethyl were allowed to act on nitrobenzene, except that 4 per cent ethylaniline was found in this case.

Taking into consideration the general result reached with nitroso-compounds, *viz.*, that negativity and reactiveness are proportional, the conclusion seems inevitable that nitrobenzene and nitroethane are differently constituted. As nitroethane is more reactive, taking up two ethyl groups where nitrobenzene barely takes up one; as nitrobenzene closely approaches azoxybenzene in its behavior towards zinc ethyl; and as nitrosobenzene acts violently under similar circumstances, we arrive concordantly at the general conclusion that nitroparaffins and nitroalphyls belong in different categories, thus:

Nitroethane,[1] $C_2H_5-N\begin{matrix}O\\O\end{matrix}$; nitrobenzene, $C_6H_5-N\begin{matrix}O\\|\\O\end{matrix}$;

and that the "spectro-chemistry of nitrogen" is not a safe guide for the present.

As to the mechanism of Bewad's reaction, nothing definite can be postulated. Zinc ethyl is undoubtedly capable of exchanging both its alkyls for a single oxygen atom, as in the case of diphenylnitrosamine. If it were possible to isolate the intermediate product which nitroethane[2] must form, the question might easily be settled, but the experimental difficulties preclude this for the time being. Perhaps it is as well to abide by what evidence we have in the nitrogen-oxygen group, and replace Bewad's interpretation by the following:

$$C_2H_5-N\begin{matrix}O\\O\end{matrix} \longrightarrow C_2H_5-N\begin{matrix}(C_2H_5)_2\\O\\O\end{matrix}Zn \longrightarrow C_2H_5-N\begin{matrix}(C_2H_5)_2\\O\end{matrix}$$

An attempt will be made to verify this hypothesis at some subsequent opportunity.

[1] This nitroparaffin formula agrees much better with Nef's conception of their salts, $CH_3CH=N\begin{matrix}O\\OMe\end{matrix}$, than with Hantzsch's: $CH_3CH\begin{matrix}-N-OMe\\|\\O\end{matrix}$.

[2] Bewad describes one of exceedingly complex composition.

The regular gradation of properties which has facilitated the study of so many series of organic compounds, and which has contributed so largely to the rapid growth of the science, is lacking in the groups under consideration. As in the tautomerism of ketones,[1] as in the behavior of acid amides,[2] so in the more intimate chemistry of nitrogen each substance is a law unto itself, and we know not to-day what the morrow may bring forth.

Experimental Part.

Diethylnitrosamine.—1.5 grams stood with 1.5 grams zinc ethyl for twenty-four days. It was recovered unaltered, and no other products could be found.

Phenylmethylnitrosamine.—9 grams each of this substance and zinc ethyl stood fourteen days in solution in benzene; on pouring into water there was violent reaction. 8.8 grams nitrosamine were recovered; the acidified aqueous solution contained traces of aromatic bases.

Diphenylnitrosamine.—The following experiment is typical: 4 grams zinc ethyl were mixed with 100 cc. benzene (sodium dried), and 6 grams nitrosamine added at one time. In a few minutes violent ebullition took place, and continued for a short while. A portion of the solution was then carefully evaporated in the cold in a current of dry carbon dioxide; a gelatinous paste remained, which when rubbed on a porous plate, solidified to a dry, yellow powder. In subsequent experiments the solution was worked up directly.

The solid addition-product shrivels between 135°–140°, is stable in dry air, and insoluble in ordinary solvents. Water and alcohol decompose it without evolution of gas.

0.2414 gram gave 0.0626 gram zinc oxide upon ignition.

	Calculated for $(C_6H_5)_2N.NO.Zn(C_2H_5)_2$.	Found.
Zn	20.8	20.3

Ten grams nitrosamine and 6 grams zinc ethyl, after reaction, were treated with just enough dilute sulphuric acid to dissolve the precipitated zinc hydrate. The benzene solution, after drying, left 8.3 grams diphenylamine (calculated

[1] Cf. Claisen: Ann. Chem. (Liebig), **291**, 45.
[2] Cf. Lachman: This JOURNAL, **18**, 600.

8.4 grams). The substance was identified by its melting-point, 54°, its boiling-point (the whole quantity distilled unchanged at 304° and 758 mm.), and by the "diphenylamine reaction."

The aqueous acid solution reduces Fehling's solution in the cold; on rendering alkaline and distilling in steam, the reducing base passes over; on neutralizing with hydrochloric acid and evaporating, ethyl chloride is given off, and but a small quantity of solid is left which gives no satisfactory results on analysis.[1]

The volatile base was determined by reduction to diethylamine.[2] 16 grams nitrosamine and 10 grams zinc ethyl were worked up as above; the acid solution was mixed with an equal volume of glacial acetic acid, and zinc dust added in small quantities until the solution no longer reduced Fehling's solution. The mixture was then filtered, made alkaline, and distilled with steam, the distillate neutralized with hydrochloric acid, evaporated to dryness, and extracted with cold alcohol. There remained 1.2 grams ammonium chloride (does not melt, nor react with nitrous acid, gives no isonitril); the alcohol left 4.3 grams diethylamine hydrochlorate on evaporation (calculated 8.8 grams). It was identified thus: conversion into the nitrosamine gave 2.5 grams boiling at 174°–175° (corr.); calculated 3.4 grams. The nitrosamine was reconverted into the hydrochlorate, and the salt finally analyzed:

0.1753 gram required 15.95 cc. (corr.) silver nitrate solution (1 cc. = 0.01088 gram Ag) for complete precipitation according to Volhard.

	Calculated for $(C_2H_5)_2NH.HCl$.	Found.
Cl	32.4	32.5

Nitrosobenzene.—The reactions were carried out in the following manner: The zinc ethyl was diluted with about four times its volume of benzene, and a saturated solution of nitrosobenzene in the same solvent added slowly, constantly cool-

[1] Cf. the similar experiences of Gürke, Ann. Chem. (Liebig), **205**, 274, and of Kjellin, Ber. d. chem. Ges., **30**, 1893.

[2] Diethylamine is not present before reduction; the solution from 16 grams nitrosamine gave no diethylnitrosamine with sodium nitrite.

ing with very cold tap water. The characteristic green color of nitrosobenzene disappears at once, but the mixture was allowed to stand several hours before working up. A considerable excess of zinc ethyl was usually taken, to insure complete reaction of the nitrosobenzene. No gas is given off on mixing the solutions. The method of procedure was simple. The benzene solution was slowly added to the calculated quantity of dilute sulphuric acid (2N), with constant cooling; after thorough shaking, each layer was filtered to remove traces of the other, and the benzene solution dried over calcium chloride.

a. Contents of the Benzene Solution.—After evaporation, cold ligroin extracts almost pure azoxybenzene (melting-point 28°, after one crystallization, 35°–36°), which is obtained in the characteristic pale-yellow needles. A dark tarry substance remains, which was not examined further. The quantity of azoxybenzene is comparatively large; thus, 10.5 grams nitrosobenzene and 15 grams zinc ethyl gave 4.7 grams neutral residue, from which ligroin extracted 2.6 grams azoxybenzene. Recalculated as nitrosobenzene, this amounts to 25 per cent of the total. Regarding the tar as polymerized nitrosobenzene,[1] we can account for an additional 20 per cent.

b. Contents of the Acid Solution.—This contains phenylhydroxylamine, small quantities of aniline and ethylaniline, and traces of other substances. No diethylaniline was found at any time. The presence of phenylhydroxylamine was shown by its reactions; the solution when warmed with potassium bichromate or ferric chloride gave the characteristic odor of nitrosobenzene, green globules forming on the sides of the test-tube. The solution also reduces ammoniacal silver at once. An indication of its quantity is given by the following facts: The acid solution from the above experiment (in which azoxybenzene was determined), was rendered weakly alkaline and distilled with steam. Volatile bases passed over, along with a red, neutral substance. By extracting the acidified distillate with ether, 1.85 grams of a red solid were obtained, which melted at 58°; it was purified by distilling in a test-tube, when it melted at 65°–66°. The substance was therefore

[1] Ber. d. chem. Ges., 31, 1513.

azobenzene,[1] which was probably formed according to the process described by Bamberger:[2]

$$\begin{matrix} C_6H_5NHOH \\ C_6H_5NHOH \end{matrix} = \begin{matrix} C_6H_5N \\ \| \\ C_6H_5N \end{matrix} + \begin{matrix} H_2O \\ H_2O \end{matrix}.$$

On the basis of this reaction there would seem to have been present 2.25 grams phenylhydroxylamine, equivalent to a minimum of 21 per cent of the original nitrosobenzene.

The accompanying volatile bases were accidentally lost; to determine their character, 12 grams nitrosobenzene and 20 grams zinc ethyl (large excess) were worked up. 3.5 grams dry base were obtained. 1.7 grams were dissolved in dilute hydrochloric acid and diazotized at 0°. The solution was extracted at once with ether,[3] the liquids quickly separated, and the ether washed with caustic soda, dried, and evaporated. 1.4 grams dark-yellow oil were obtained, which gave Liebermann's reaction with phenol and concentrated sulphuric acid; it solidifies on cooling, and melts again at about 12°.[4] This corresponds to 2.4 grams total ethylaniline, a yield of 14 per cent (calculated 16.8 grams). After extracting the nitrosamine, the diazotized solution was made alkaline and again extracted with ether; the ether contained mere traces of a red substance. A blank test showed that less than 0.1 gram dimethylaniline can be identified by this reaction. Diethylaniline was therefore absent. The aniline still present in the alkaline solution (as diazobenzene) was not estimated (its presence was shown with β-naphthol); by difference it is found to be 1.1 grams.

Computing the various substances obtained in this reaction in terms of nitrosobenzene, a total of 92 per cent is found as a minimum, without taking account of inevitable losses in

[1] On one occasion azoxybenzene appeared at this stage.

[2] Ber. d. chem. Ges., **27**, 1550.

[3] The following simple device may be recommended when a freezing-mixture is not at hand: The acid solution is covered with a layer of ether in a filtering-flask, and a current of air forced through both liquids. The temperature rapidly sinks below 0°. A solution of sodium nitrite is then slowly added. The nitrosamine thus comes into immediate contact with ether, and is at once removed from further action without risk of loss or rise in temperature.

[4] This melting-point is approximate; the nitrosamine of methylaniline melts at 17°.

manipulation. This in itself is a sufficient guarantee that nothing of importance has been overlooked.

Azoxybenzene.—2 grams were allowed to stand in solution in benzene with 3.5 grams zinc ethyl. After fourteen days, 1.8 grams were recovered.[1] Azoxybenzene is one of the substances which gave an interesting reaction on warming with zinc ethyl; details will be published later.

Dimethylnitramine.—3.5 grams stood nineteen days in ether solution with 5 grams zinc ethyl. On pouring into ice-cold dilute sulphuric acid, and extracting six times with ether, 3.4 grams were recovered.

Nitroethane.—At first Bewad's[2] directions were followed; a modification which is more expeditious will be described later. 24 grams nitroethane and 46 grams zinc ethyl were allowed to stand sixteen days in ether solution. 3.1 grams triethylamine oxide were obtained as a perfectly colorless oil boiling between 157°–158° (753 mm.) without decomposition.[3] Calculated for 24 grams nitroethane, 39 grams. However, 7 grams nitroethane were recovered, making a total yield of 12 per cent triethylamine oxide.

Bewad's results with 2 molecules of zinc ethyl were not confirmed. 20 grams nitroethane and 63 grams zinc ethyl stood in 100 cc. ether for fourteen days. 7 grams triethylamine oxide were obtained (25 per cent of the calculated yield). The neutral residue contained about 2 grams nitroethane; Bewad's substance boiling at 178°–180° could not be found.

Nitrobenzene.—9 grams each nitrobenzene and zinc ethyl stood in solution in ether for fifteen days. Practically no gas was evolved on pouring into ice-cold dilute sulphuric acid. The acid solution was treated as in the case of nitrosobenzene. A small amount of phenylhydroxylamine was found, (quantity not accurately determined: estimated at 0.5 gram), and mere traces of aniline and ethylaniline; no diethylaniline was present. The neutral ether solution left a dark oil, which was distilled with steam; the distillate was collected in ether and fractioned; 4.5 grams nitrosobenzene (boiling-point 210°-

[1] This slight deficit was caused by the occasional removal of a small quantity to note the progress of the reaction.

[2] *Loc. cit.*

[3] The properties of triethylamine oxide will form the subject of a separate communication.

215°) were recovered,[1] amounting to 50 per cent of the original material. The residue weighed 3.4 grams, forming a dark-red, sticky mass, which did not solidify at —20°; nothing tangible could be extracted from it.

Practically identical results were obtained from the use of 2 molecules of zinc ethyl. 7 grams nitrobenzene stood with 14 grams zinc ethyl as above. There were obtained 0.35 gram ethylphenylnitrosamine (equivalent to 4 per cent of the theoretical quantity of ethylaniline), 3.5 grams nitrobenzene, and 2.7 grams non-volatile tarry residue.

The Preparation of Zinc Ethyl.—The large quantities of zinc ethyl needed for the above experiments were manufactured according to the modified Gladstone–Tribe process described by me some time ago.[2] The following additional data will demonstrate the advantages of this method as to convenience and yield. 650 grams ethyl iodide were worked up in seven successive portions. 201 grams redistilled zinc ethyl of constant boiling-point were obtained, with about 15 grams material boiling at a lower temperature; calculated yield 256 grams. Time, five hours. 300 grams ethyl iodide were employed in a single operation; yield, 92 grams redistilled zinc ethyl and 3 grams lower-boiling products (calculated, 108 grams). Time, one hundred and ten minutes.

EUGENE, OREGON, March, 1899.

REVIEWS AND REPORTS.

Gases of the Atmosphere.

The German Chemical Society, from time to time, invites chemists who are engaged in work on special lines in which they are recognized as authorities, to lecture before the Society upon their specialties. Among those who have been thus honored are Victor Meyer,[3] who lectured on Stereochemistry; Emil Fischer,[4] on Syntheses in the Sugar Group; O. Wallach,[5] on Terpenes and Camphor; Lothar Meyer,[6] on Inorganic Chemistry According to the Periodic System of the Elements; J. H. van't Hoff,[7] on Theory of Solutions; R.

[1] And about 0.5 gram higher boiling oily residue.
[2] This JOURNAL, **19**, 410.
[3] Ber. d. chem. Ges., **23**, 567.
[4] *Ibid.*, **23**, 2114.
[5] *Ibid.*, **24**, 1525.
[6] *Ibid.*, **26**, 1230.
[7] *Ibid.*, **27**, 6.

Fittig,[1] on Unsaturated Acids; Th. Curtius,[2] on Hydrazines and Triazoic Acid; Robt. Hasenclever,[3] on the Development of the Soda Industry in the past Twenty-five Years; Cl. Winkler,[4] on The Discovery of New Elements; M. Maercker,[5] on Agricultural Chemistry; W. Nernst,[6] on Electrolytic Decompositions of Water Solutions; H. Bunte,[7] on Illumination; and M. Delbrück,[8] on Fermentation. Professor Wm. Ramsay,[9] in response to an invitation from the Society, delivered a lecture in this series on Dec. 19, 1898, upon a subject with which his name will ever be associated, that of "The Newly Discovered Gases and Their Relation to the Periodic System." The lecture was illustrated by photographic projections of the apparatus and exhibitions of the spectra of the gases. While in Berlin, Professor Ramsay gave a private lecture before the Emperor and his family, and also delivered a public lecture upon the same subject. A number of interesting points, which have probably not before been mentioned, were brought out in this lecture before the Society. Prof. Ramsay called attention to the fact that the present arrangement of the periodic system will not accommodate the element argon, with an atomic weight of 40, which should follow potassium; but the fact that the element with higher atomic weight comes first need not destroy our faith in the general arrangement of the system, for the recent work on tellurium has shown its atomic weight to be 127.6, although it precedes iodine with an atomic weight of 126. If the atomic weight of helium is 4 and that of argon 40, there should be, if the usual relation exists between the members of the series, an element with an atomic weight about 16 greater than helium and 20 less than argon. This can be seen from the following arrangement:

H — 1						
Li — 7	Be — 9.2	B — 11	C — 12	N — 14	O — 16	
Na — 23	Mg — 24	Al — 27	Si — 28	P — 31	S — 32	
			He — 4			
		F — 19	(?) — 20			
		Cl — 35.4	A — 40			

The apparently hopeless task which Prof. Ramsay undertook was to find this missing element, and it is to such an incentive and the work it led to that we owe the discovery of krypton, neon, metargon, and xenon. As suggested

[1] Ber. d. chem. Ges. **27**, 2658.
[2] *Ibid.*, **29**, 759.
[3] *Ibid.*, **29**, 2861.
[4] *Ibid.*, **31**, 6.
[5] *Ibid.*, **31**, 464.
[6] *Ibid.*, **31**, 1547.
[7] *Ibid.*, **31**, 5.
[8] *Ibid.*, **31**, 1913.
[9] *Ibid.*, **31**, 3111.

by the occurrence of helium, all known minerals were tested, but without result. The nitrogen absorbed by magnesium and the ammonia formed from it were thoroughly studied with similar negative results. All attempts to separate substances from argon by diffusion also failed. Although these negative results can be so briefly mentioned they could only be determined by an immense amount of work requiring many months and the greatest skill. When nearly all the possible methods had been tried Ramsay conceived the idea of applying the method of fractional evaporation to the liquefied argon. The argon was liquefied by the use of liquid air, and when most of this air had evaporated it seemed, he said, a pity not to examine the residue. It was the investigation of this which led to the discovery of krypton,[1] the method of isolation and properties of which have already been described. This proved to be the missing element with the atomic weight 22. As also described in the previous note,[1] neon and metargon were found in the fractions from the liquid argon. The neon was always mixed with helium and argon and, as their solubility in ordinary solvents was very slight, they were dissolved in liquid oxygen. By fractional evaporation and removal of the oxygen the neon was obtained in pure condition. To give some idea of the skill and care required for this work, it will only be necessary to give the quantities used to determine the physical constants. The volume of the gas at a pressure of 250 mm. was 30 cc., and the weight of this was 0.0095 gram. An investigation showed that the small amount of these gases present in the argon had no effect on its properties, as the densities of the impure and purified material were 19.94 and 19.96, respectively. They were unable to detect, by the methods available, the presence of xenon by examining 15 liters of argon. J. ELLIOTT GILPIN.

Artificial Indigo.

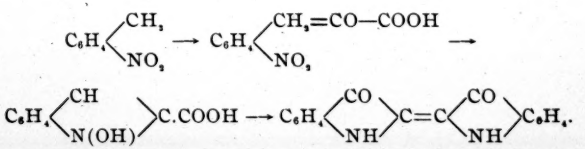
During the past twenty years scientific and commercial circles have been disturbed by periodical reports of the results which it was predicted would follow the discovery of a practical synthetical method for the preparation of indigo, a discovery which would cause serious injury to the vast interests engaged in the preparation of the natural product. Just as the threatened overthrow of the kelp industry by the improved methods of extracting iodine from Chili salpeter, led to the introduction of modern scientific methods in place of those which had been used for years; so the conditions in the indigo industry adjusted themselves to circumstances and the

[1] This JOURNAL, **20**, 696.

natural product continued to hold its own. Since the introduction, early in the eighties, of artificial indigo, each step in the improvement and reduction in the price of this article has been met by a similar change in the natural product. This has been due mainly to two causes, an improvement in the methods of obtaining the crude material, and the introduction of cheaper methods of transportation. A method which threatened to affect the industry to a marked degree, was rendered unprofitable by the application of scientific methods in the extraction of the crude dye-stuff and a study of the exact conditions of fermentation, which made it possible to increase the yield to a remarkable degree. By such methods the price of indigo has been greatly reduced, and we are now in one of those periods when it seems as if the time had at last arrived when the natural product can no longer shut out the artificial product, but will be forced to divide the field with it. In the case of all the older methods for the preparation of indigo the difficulties to be overcome have been the cost of the substance from which the indigo is made and the small yield of the dye-stuff. Let us review briefly the history of the production of artificial indigo. Von Baeyer discovered several methods for the preparation of indigo, the most important being the method in which *o*-nitrophenylpropiolic acid is treated with a reducing agent, forming indigo, carbon dioxide, and water, according to the following equation:

$$2C_6H_4(NO_2)C{\equiv}C.COOH+2H_2 = C_{16}H_{10}N_2O_2+2CO_2+2H_2O,$$

and the one in which *o*-nitrobenzoic aldehyde in acetone is treated with alkalies. In 1897 Reissert[1] found that *o*-nitrotoluene with the ester of oxalic acid would form *o*-nitrophenylpyroracemic acid, and that the latter by reduction passed to N-oxindolcarbonic acid which can readily be converted into indigo. These changes can be graphically represented as follows:



In another method discovered by Blank[2] a few months ago, the indoxylic ester which Von Baeyer had shown could easily be converted into indigo, was prepared by starting with aro-

[1] Ber. d. chem. Ges., **30**, 1030.
[2] *Ibid.*, **31**, 1812.

matic amines and esters of chlormalonic acid. From these was obtained an aliphatic aminomalonic acid ester, which by loss of alcohol forms the indoxylic acid ester:

$$C_6H_5NH_2+CHCl(COOC_2H_5)_2 = C_6H_5NHCH(COOC_2H_5)_2+HCl,$$

$$C_6H_5NHCH(COOC_2H_5)_2 = C_6H_4\begin{cases}NH\\CO\end{cases}CHCO_2C_2H_5 + C_2H_5OH,$$

$$C_6H_4\begin{cases}NH\\CO\end{cases}CHCO_2C_2H_5 + H_2O = C_6H_4\begin{cases}NH\\C(OH)\end{cases}=CH + CO_2 + C_2H_5OH,$$

$$2C_6H_4\begin{cases}NH\\C(OH)\end{cases}=CH + 2O = C_6H_4\begin{cases}NH\\CO\end{cases}C=C\begin{cases}NH\\CO\end{cases}C_6H_4 + 2H_2O.$$

Just what results these methods will give so far as the production on the large scale is concerned cannot yet be determined; but in the meantime the Badische Anilin- und Soda. fabrik[1] have introduced a synthetical indigo under the name "Indigo rein," which is being manufactured in large quantities, and sold at a price which enables it to compete with the natural product.

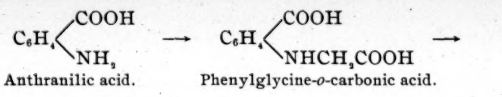
In 1890 Heumann,[2] in attempting to prepare indoxyl, $C_6H_4\begin{cases}NH\\C(OH)\end{cases}=CH$, by heating phenylglycine with dehydrating agents, used sodium hydroxide, and obtained a yellow liquid which, on exposure to the air, gave indigo. In order to prevent the formation of isomers of indoxyl he later used anthranilic acid and obtained by treating this with chloracetic acid, phenylglycine-*o*-carbonic acid:

$$C_6H_4\begin{cases}NH_2\\COOH\end{cases} + CH_2ClCOOH = C_6H_4\begin{cases}NHCH_2COOH\\COOH\end{cases} + HCl.$$

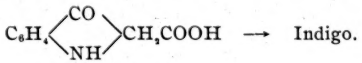
The method finally adopted for transforming this compound into indigo was to heat to 200° with an alkali, dissolve in

[1] Chem. Centralblatt, 1891, I, 560; II, 144.
[2] Ber. d. chem. Ges., **23**, 3043; **23**, 3431.

water, and oxidize by forcing air through the solution. It is this method which, according to the best information available, is used by the Badische Anilin- und Sodafabrik for manufacturing the "Indigo rein." The changes can be represented thus:

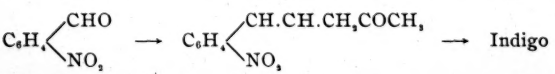


Anthranilic acid. Phenylglycine-*o*-carbonic acid.

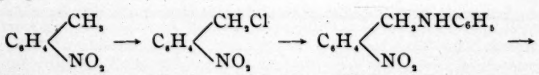


Indoxylcarbonic acid.

The transformation of anthranilic acid into indigo can be quite readily and economically carried out, but as the anthranilic acid is obtained from phthalic acid and that in turn from naphthalene, the price at which the indigo can be put on the market depends to a great extent on the relative price of these products. The Badische Anilin- und Sodafabrik[1] have recently patented a process for obtaining phthalic acid from naphthalene by heating with sulphuric acid to 200°. Under these conditions the acid acts as an oxidizing agent, and although the price of the acid has been lowered by this method, perhaps cheaper methods may be discovered for preparing the anthranilic acid. In an address[2] delivered before a Section of the International Congress of Applied Chemistry last July, Prof. P. Friedlaender suggested the possibility of using a method discovered by Von Baeyer and Drewsen. The starting-point is *o*-nitrobenzoic aldehyde, which is converted into *o*-nitrophenyllactic acid ketone, and this in turn into indigo:

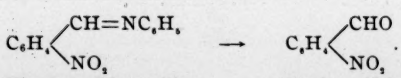


This cannot be a commercially successful process unless the price of the *o*-nitrobenzoic aldehyde is reduced, and this may be possible as patents have recently been taken out for its preparation from *o*-nitrotoluene:



o-Nitrotoluene. *o*-Nitrobenzylchloride. *o*-Nitrobenzylaniline.

[1] Chem. Ztg., 1897, **21**, 291. [2] *Ibid.*, 1898, **22**, 622.



o-Nitrobenzylideneaniline. *o*-Nitrobenzaldehyde.

The fact of its preparation and introduction in competition with the natural product raises a number of questions as to the relative value of the two products and their use under different conditions and with different materials.

Natural indigo contains the following constituents: Indigo blue 29–30 per cent, indigo red 2–10 per cent, indigo brown 1–6 per cent, indigo gelatin 2–5 per cent, ash 3–20 per cent, and water 3–6 per cent. The artificial indigo contains 97 per cent of indigo blue, the rest consisting of salts and water. It contains no indigo red or indigo gelatin. As to the relative effect of the presence or absence of these constituents there is a great diversity of opinion.

Sigismund Lang,[1] from his observations as a chemist connected with one of the European factories and as Indigo Commissioner, considers the indigo red a necessary ingredient to facilitate the fixing of the dye. He says the dyer values his indigo according to the relative amount of indigo red, the amount desired varying according to the material to be dyed. He ascribes the poor quality of the Java indigo to the small proportion of indigo red present. As the Java indigo is useless from this cause, he therefore argues that "Indigo rein" will be likewise, from the same cause. He acknowledges that the artificial product dyes rapidly, but claims it is not a fast color, and points to the fact that the manufacturers recognize the absence of fixing material in the artificial product as they recommend the use of Turkey-red oil as a fixing agent. Indigo gelatin plays very much the same rôle as the indigo red, but to a less degree.

Carl Bucher,[2] on the other hand, claims that the rôle of the indigo red has been greatly overestimated. It mainly affects the shade of the dye. The indigo white permeates the substance, and is there changed to indigo blue, but the indigo red does not permeate the material to the same degree as the indigo white. The rôle which the indigo gelatin plays can be better taken by the Turkey-red oil, as it causes the rapid absorption of the dye-stuff by the material. The presence of one of these fixing-agents is necessary in dyeing cotton; but not only are they not necessary in the case of wool, but they may be objectionable, and for such work the introduction of this pure substance may prove of great value,

[1] Chem. Ztg., 1897, **21**, 961. [2] *Ibid.*, 1897, **21**, 1005.

as its action can be regulated, and results obtained with it which could not be obtained with the impure mixture of the natural product. The field from which the natural indigo has been driven by other dye-stuffs may now be reclaimed by the pure indigo.

An investigation by Binz and Rung[1] showed that 87.89 per cent of the dye-stuff was fixed on the fabric. The artificial product comes in two forms, as a paste and as a powder. It saves all labor of grinding, and the dyeing process can be easily controlled and regulated. It has proved very successful in calico printing; the stamping is clear, and the change into isatin takes place readily. It is now used for making indigo extract and carmine, and the process of testing and valuing is greatly simplified. In 1897 the price of the natural indigo, calculated per kilogram of indigotin, was 12.50–16.50 marks, depending upon the quality, while the artificial was worth 17 marks. The present price of the latter is 16 marks.

An unbiased investigator, after studying the arguments for and against this substance, cannot fail to be impressed with the idea that it has an important rôle to play, and that while it will probably never entirely drive out the natural product yet it will be found more useful for certain purposes than that product, even though it may be more expensive.

J. Elliott Gilpin.

Fermentation without Cells.

In a note in Vol. 20 of this Journal, page 699, an abstract of Edward Buchner's work is given under the above title. The conclusions reached were that alcoholic fermentation is possible without cells, and that fermentation is probably caused by an enzyme which is dissolved in the liquid within the cell of the living yeast, and can be obtained, mixed with other substances, by crushing the cells and expressing the liquid contents.

In Sept., 1898, H. Abeles,[2] of Vienna, opposed Buchner's enzyme theory, offering instead what may be called the plasma hypothesis. Abeles thinks that the fermenting action of yeast juice is due to the presence of living fragments of protoplasm, torn from the cells, which have passed through the filter; he claims that his experiments prove that substances which are toxic to yeast, such as sodium metarsenite, ammonium fluoride, chloroform, or glycerin, if added to yeast juice in sufficient quantity, are equally toxic to the latter, which he thinks would not be true if the fermenting agent were an enzyme.

[1] Ztschr angew. Chem., 1898, 957. [2] Ber. d. chem. Ges., 31, 2261.

Buchner's report of his recent experiments and his reply to Abeles is in the *Berichte* of January 23, 1899. He says that if the plasma hypothesis is correct, yeast juice subjected to centrifugal motion would separate into an upper layer containing few solid particles of plasma and hence possessing little fermenting power, and a lower layer and sediment containing most of the solid particles of plasma, and hence possessing great fermenting power. His experiments show that after hours of centrifugal motion both layers excite fermentation to the same extent. In another series of experiments Buchner shows that the activity of dried yeast juice is not lessened by keeping it for two months. This could scarcely be true of dried living protoplasm. He then repeats the experiments of Abeles with glycerin and chloroform. Assuming that Abeles had not taken care to bring the yeast particles into thorough contact with these reagents, Buchner provides for this in arranging his apparatus. It is known that glycerin and chloroform dissolve enzymes without injury, but kill living organisms. In parallel experiments the fermenting power of dried yeast juice and of fresh yeast in the presence of an excess of these reagents was tested. Equivalence in the amounts of yeast and of dried yeast juice used was secured by determining the nitrogen in each; their fermenting power was found in all cases to be identical, showing, Buchner claims, that while both the glycerin and the chloroform had killed the yeast, stopping further growth, it had not injured the enzyme present in the yeast cells.

Buchner grants that Abeles is right in saying that mercuric chloride, ammonium fluoride, and sodium metarsenite are as toxic to yeast juice as to the living yeast, but says that these reagents form precipitates, chemical compounds, with the albuminates of the yeast or yeast juice, and probably form chemical compounds with the enzyme; hence they cannot be used to decide between the enzyme and plasma hypotheses in the way in which glycerin and chloroform, which do not form albuminate compounds, may be used. In conclusion, Buchner repeats with great care experiments on heating yeast and yeast juice. Yeast is killed when heated six hours at 85°. Yeast juice was heated eight hours at 85° without impairing its fermenting power.

It would seem that Buchner has established his theory as far as is possible without isolating the zymase; work in this direction is going on under his guidance. In the meantime, A. Wróblewski, of Cracow (without consulting Buchner), has been studying the properties of yeast juice by the method of fractional coagulation. A part of the juice coagulates at 35°, another at 41°, others at 51°, 56°, 59°, 62°, and 68°. The coagu-

lated part does not pass through a Chamberland filter. The filtrate from the coagulate at 35° ferments sugar; the filtrate of the coagulate at 41° does not; hence, Wróblewski assumes that the enzyme "zymase" is in that portion of the yeast juice which coagulates at 41°. He further notes that the albuminate coagulating at 41° is the first to be destroyed by the proteolytic enzymes present in the yeast juice.

Whether the enzyme theory is established or not, certainly Buchner's work has shown the assumption of Abeles to lack foundation. Indeed, it would require positive evidence to lead chemists or biologists to accept the idea of living fragments of plasma, of bits torn from cell walls, acting like living organisms. E. R.

Report of the Committee on Atomic Weights of the German Chemical Society.[1]

At a meeting of the executive committee of the German Chemical Society, held on the first of December, 1897, the question was put to them by a commission of analytical chemists, who were meeting at that time in Berlin, which atomic weights should be adopted as a basis for practical analytical calculations.

On motion of Dr. E. Fischer, a commission composed of H. Landolt, W. Ostwald, and K. Seubert was appointed to prepare a report on this subject. The commission, after much preparatory labor, held two meetings at which the selection of a unit for the atomic weights, as well as the values for the individual elements, were thoroughly discussed. Finally they decided unanimously to present the following propositions:

I. *As a basis for the computation of atomic weights, the atomic weight of oxygen shall be taken to be equal to 16.000, and the atomic weights of the other elements shall be computed on the basis of ratios to oxygen, whether determined directly or indirectly.*

II. *As atomic weights of the elements, for practical use, the following most probable values, at this time, are proposed:*

Aluminium	Al	27.1	Boron	B	11.
Antimony	Sb	120.	Bromine	Br	79.96
Argon(?)	A	40.	Cadmium	Cd	112.
Arsenic	As	75.	Caesium	Cs	133.
Barium	Ba	137.4	Calcium	Ca	40.
Berylllium	Be	9.1	Carbon	C	12.00
Bismuth	Bi	208.5*	Cerium	Ce	140.

[1] Ber. d. chem. Ges., 31, 2761 (1898).

Chlorine	Cl	35.45	Phosphorus	P	31.0
Chromium	Cr	52.1	Platinum	Pt	194.8
Cobalt	Co	59.	Potassium	K	39.15
Copper	Cu	63.6	Praseodymium(?)	Pr	140.
Erbium(?)	Er	166.	Rhodium	Rh	103.0
Fluorine	F	19.	Rubidium	Rb	85.4
Gallium	Ga	70.	Ruthenium	Ru	101.7
Germanium	Ge	72.	Samarium(?)	Sm	150.
Gold	Au	197.2	Scandium	Sc	44.1
Helium(?)	He	4.	Selenium	Se	79.1
Hydrogen	H	1.01	Silicon	Si	28.4
Indium	In	114.	Silver	Ag	107.93
Iodine	I	126.85	Sodium	Na	23.05
Iridium	Ir	193.0	Strontium	Sr	87.6
Iron	Fe	56.0	Sulphur	S	32.06
Lanthanum	La	138.	Tantalum	Ta	183.
Lead	Pb	206.9	Tellurium	Te	127.
Lithium	Li	7.03	Thallium	Tl	204.1
Magnesium	Mg	24.36	Thorium	Th	232.
Manganese	Mn	55.0	Tin	Sn	118.5*
Mercury	Hg	200.3	Titanium	Ti	48.1
Molybdenum	Mo	96.0	Tungsten	W	184.
Neodymium(?)	Nd	144.	Uranium	U	239.5
Nickel	Ni	58.7*	Vanadium	V	51.2
Niobium	Nb	94.	Ytterbium	Yb	173.
Nitrogen	N	14.04	Yttrium	Y	89.
Osmium	Os	191.	Zinc	Zn	65.4
Oxygen	O	16.00	Zirconium	Zr	90.6
Palladium	Pd	106.			

The following facts are to be noted with regard to the table. The numbers, in general, are given with only so many decimal places that the last one may be regarded as sure; consequently the atomic weights determined by Stas to within 3–6 units in the third decimal place are given with two decimals. The better determined atomic weights besides these, with one decimal, and all less surely determined ones with no decimals. The only exceptions to this rule are nickel, bismuth, and tin, which are marked with an asterisk. In the case of nickel the exception is made to emphasize the undoubted difference between the atomic weights of nickel and cobalt. That of cobalt is almost surely 59.0 and the possible variation from this value is not greater than ± 0.2. The atomic weight is surely smaller than that of cobalt, although the value 58.7 is not guaranteed within ± 0.2. In order then not to make it appear, through rounding off to 59, that nickel and cobalt have the same atomic weight, the most probable atomic weight, Ni = 58.7, is given.

As regards bismuth and tin, the true atomic weights lie probably nearer the values ending in 0.5 than to the whole numbers, although they are not definitely known to within 0.1.

For hydrogen the value 1.008 is to be considered as fixed to within 0.001, but for practical purposes the rounding off to 1.01 is allowable as this change signifies an error of only one-fifth of 1 per cent. The elements whose names are followed by a question mark (?) are uncertain either in regard to their homogeneity or as to whole units in their atomic weights.

Some of the arguments which led to the above conclusions are given by each member of the commission with remarks.

The arguments are in no way new, and mostly historical. As Prof. Ostwald says, "all will agree that there is only one question as to a basis, that between oxygen and hydrogen, and historically no other element has been suggested."

The strongest argument for oxygen is that it forms compounds with almost all other elements, thus rendering direct experimental determination possible, whereas with hydrogen almost all determinations depend upon the ratio between oxygen and hydrogen, or its multiples.

There is a pressing need for a generally adopted atomic weight table, since in various chemical works figures appear which not only differ from each other on account of the unit adopted but even where the same basis is used differences will be found for one and the same element.

In Germany we have at the same time the tables of L. Meyer and K. Seubert on the one hand and that of Ostwald on the other, while in America we have the annually appearing table by F. W. Clarke.[1] In consequence of this state of affairs such uncertainty has arisen as to introduce serious inconvenience in analytical calculation.

It is proposed to issue this table every year with the first number of the *Berichte*, after it has been revised to suit the changes which the work of the year may render necessary.

It is certainly very desirable that an international understanding in this matter should be reached. There should be no serious difficulty about this seeing how few serious differences there are between the figures of Clarke, of Richards,[2] and those of the above table.

C. L. REESE.

[1] J. Am. Chem. Soc., **20**, 163 (1898).

[2] This JOURNAL, **20**, 543 (1898).

A DIGEST OF METABOLISM EXPERIMENTS IN WHICH THE BALANCE OF INCOME AND OUTGO WAS DETERMINED. By W. O. ATWATER, Ph.D., AND C. F. LANGWORTHY, Ph.D. Prepared under the supervision of A. C. TRUE, Ph.D., Director of the Office of Experiment Stations. Bulletin No. 45 (Revised Edition). U. S. Department of Agriculture, Office of Experiment Stations.

This work aims to give as complete a digest as possible of all experiments which have been carried on to determine the income and outgo of the animal organism, whether matter or energy. In most cases the balance of nitrogen and carbon was determined, but a number of experiments include phosphorus, sulphur, or other mineral matter. The balance of nitrogen and energy has been determined in a few cases only. A total of 3,661 individual tests or averages is included, 2,299 of which were made with man, the remainder with cattle, horses, sheep, dogs, poultry, doves, etc. The nitrogen balance was determined in 2,234 tests with man, and 1,156 with animals; the balance of carbon and nitrogen in 65 with man and 206 with animals. No attempt was made to include experiments published since 1894. The work purposes to give a brief epitome of the objects and results of individual experiments; tables furnish the framework for this, and supplementary data are given in the accompanying text. The tables are classified first according to the animal, next the balance of nitrogen, as nitrogen and carbon, or nitrogen and energy, and finally subdivided according to the conditions of the experiment. It will be of great assistance to all engaged in investigations on the chemistry and economy of foods. G. S. F.

NEUE GASOMETRISCHE METHODEN UND APPARATE. VON OTTO BLEIER. Spielhagen and Schurich: Wien. 1898.

The author is well known through his many and excellent improvements in gas analytical apparatus and methods, accounts of which have appeared from time to time in the *Berichte* of the German Chemical Society. The present work is mainly concerned with the applications of these improvements to the analysis of gases, though considerable attention is given to the description and discussion of the already existing apparatus and operations which are affected by the author's own inventions and suggestions.

According to the preface, it was the author's first intention to produce an elaborate work which should incorporate his own improvements, and at the same time give a complete summary of the present condition of gasometry. This purpose could not, however, be realized owing to the pressure of other duties. He therefore decided to present, in its incomplete form, the material already collected. This explanation will sufficiently account for the somewhat uneven character of the different parts of the work. H. N. M.

THE ELEMENTS OF PHYSICAL CHEMISTRY. By J. LIVINGSTON R. MORGAN, Ph.D., of the Department of Physical Chemistry, Columbia University. First Edition, First Thousand. New York: John Wiley Sons; London: Chapman and Hall. 1899. pp. 299.

The author states that "the object of this book is to present the elements of the entire subject of physical chemistry in one volume, together with the important and but little known applications of it to the other branches of chemistry." The work treats of the solid liquid, and gaseous states of matter, of solutions, rôle of the ions in analytical chemistry, thermochemistry, chemical equilibrium and kinetics, the phase rule, and electrochemistry.

Even considering the very elementary character of the book one is impressed by the entire omission of a number of important chapters. Under liquids no mention is made of Kopp's work on atomic volumes, of the work of Pulfrich, Landolt, Gladstone, Brühl, and others on the refractivity of liquids, of the rotation of the plane of polarized light and the Le Belvan't Hoff hypothesis, of the work of Perkins and of Rodger and Watson on magnetic rotation, of Thorpe and Rodger on viscosity, of Ramsay and Shields on the surface-tension of liquids as applied to the determination of molecular weights.

The chapter on solutions contains much of value, but in places is not quite accurate. From page 83 one would conclude that artificial semi-permeable membranes were discovered by Pfeffer, when the discovery belongs to Traube. On page 85 we find "equal amounts of solute," instead of equivalent amounts. The boiling-point and freezing-point methods of Beckmann are described, and no mention is made of the large amount of subsequent work, which has greatly improved both of them.

The dilution law of Ostwald is considered (p. 170), while the more recently discovered law of Rudolphi is not mentioned. The latter, although purely empirical, holds as well for the strongly dissociated electrolytes, as the former for the more weakly dissociated, and is probably of equal importance.

The subject of solid solutions seems to merit more than eight lines even in a very elementary book.

The discovery of the relation between the dielectric constants of solvents and their dissociating power is ascribed solely to Nernst, while, in fact, it was pointed out at the same time by J. J. Thomsen. (Phil. Mag., 36, 320.)

The author seems to have drawn for his material rather upon text-books which have been published several years, than upon the current literature; hence some of the omissions.

The reader of the book will be able to obtain an elementary conception of many of the fundamental principles which underlie the science of physical chemistry. HARRY C. JONES.

CORRESPONDENCE.

BERLIN, March 30, 1899.

TO THE EDITOR:

With a view to securing agreement in the atomic weights to be used for practical purposes, the German Chemical Society submitted the question for investigation to a Commission and in accordance with its report, has adopted the resolutions appended. The most essential points are these: Oxygen with the value 16.000 shall be taken as the basis of calculation, and for practical purposes the atomic weights shall be expressed with only so many decimal places, that the last can be accepted as correct.

The German Chemical Society is conscious that the task which it set has received only a partial solution, and that the work must be carried forward until agreement in this question prevails in all civilized countries. While it is perhaps not to be expected that agreement will be reached in the recalculation of all the available material and the validity of the atomic weights established to the last decimal place, it seems possible to carry out the more modest task of obtaining agreement in the atomic weights employed in analytical and technical work.

We take the liberty of inviting the chemical Societies and similar Institutions of all countries to assist in the formation of an International Commission, whose task it shall be, to settle this question, either by means of written communications or by personal conference. We would first propose that every Society should elect members, whose names shall be sent to the President of the German Commission, Prof. Dr. Landolt, Berlin NW., Bunsenstrasse 1. As soon as answers to this invitation are received the preparatory steps in the work of the International Commission will be taken. In the meantime the Societies which have accepted the invitation will be advised of the progress of the matter.

The Members of the German Commission on Atomic Weights: H. Landolt, W. Ostwald, K. Seubert.

Corrections.

Vol. 20, page 327, line 14: *For* "triaxial" *read* "biaxial."

Vol. 20, page 338, line 14 from bottom: *For* "triaxial" *read* "biaxial."

Vol. 21, page 256, line 8: *For* "attainable" *read* "obtainable."